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International Conference on Physics

London 1934

A JOINT CONFERENCE ORGANIZED
BY THE INTERNATIONAL UNION OF PURE
AND APPLIED PHYSICS

AND
THE PHYSICAL SOCIETY

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In two volumes

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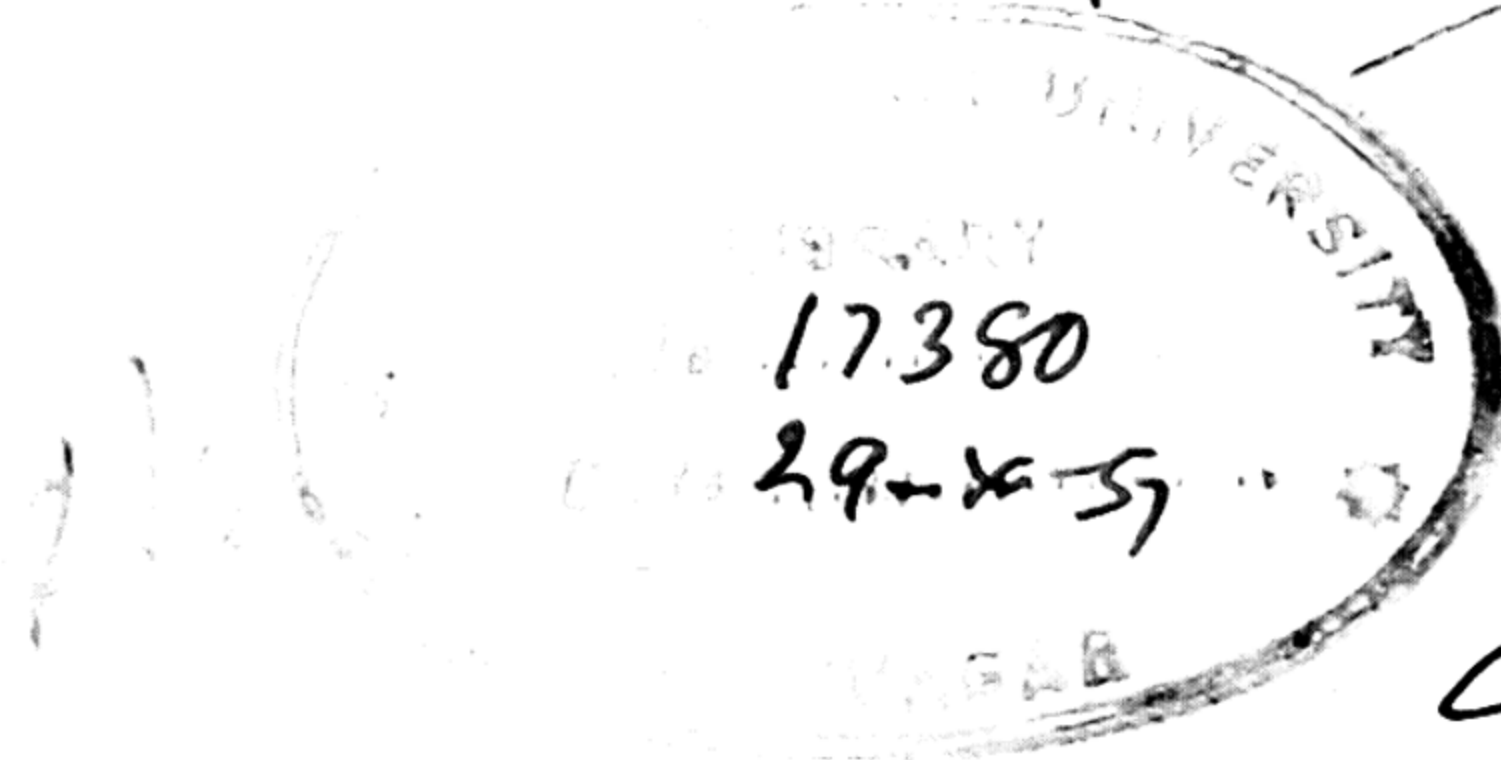
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PREFACE

THE INTERNATIONAL CONFERENCE ON PHYSICS (1934) was organized by the International Union of Pure and Applied Physics and the Physical Society.

Some 200 distinguished physicists attended either as delegates of the National Committees adhering to the Union or as guests of the Conference, invited by the joint Presidents. In addition, membership was open to all interested in Physics; the roll of members contained over 600 names.

The meetings in London were held either in the rooms of the Royal Society, Burlington House, or at the Royal Institution of Great Britain.

The Conference also met at Cambridge on Thursday, October 4th, by the invitation of Lord Rutherford.

The papers read before the Conference, with contributions to the discussions made either at the meetings or subsequently, are being published in full in two volumes:

Vol. I. Nuclear Physics.

Vol. II. The Solid State of Matter.

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OPENING SURVEY

By SIR W. H. BRAGG, O.M., F.R.S.

THE importance and interest of those phenomena of the Solid State which are to be considered at this meeting of the International Union of Physics are most agreeably emphasized by the largeness of the attendance and by the presence of so many recognized authorities. Especially may we congratulate ourselves on the fact that well-known investigators have come to us from many countries, from America in the West which gives us our President Dr Millikan to Russia in the East which sends us representatives of the distinguished staff directed by Dr Joffé in Leningrad.

This is by no means the first conference that has discussed the problems of the Solid State. At the root of all physical and chemical advance lies the urgent need for fuller understanding of the forces that bind atoms and molecules together. In recent years we have acquired new powers of examining the structure of the solid and of observing the action of the atomic forces under new conditions. The consequent growth of knowledge has been rapid, and it is not surprising that successive Conferences have met to discuss it and to co-ordinate it. The promoters of this Conference have believed that there is again the need and the opportunity for a further review: their belief is already fully justified by the excellence of the papers that have been prepared and are now in our hands.

It has been thought well to arrange the subjects for discussion into two groups. In the one, consideration will be given to certain physical phenomena which are characteristic of the Solid State: the other will consider the efforts to apply mathematical analysis to observed facts. I have been asked to make a preliminary statement which will explain in general terms the significance of the advances that are being made in each of these directions.

Twenty years ago it was discovered that the arrangement of the atoms in a crystal might be examined by the use of X-rays. The new method was eagerly applied to the determination of crystalline structures of all kinds. One of the most striking facts revealed in the course of the search was the wide prevalence of the crystalline structure: it had not been previously realized that the regularity of arrangement characteristic of

the crystal is a normal condition of the solid body. The X-rays had something to tell of the constitution of substances of all kinds: not merely of those that are obviously crystalline, nor only of those that under special circumstances look to be crystalline, such as the metals, but also of such apparently amorphous substances as woods and vegetable fibres generally, of the materials of the living world, the cell wall, nerve and muscle, hair and wool.

During these twenty years of intensive research certain very important facts have become gradually more clear. One of them is the extreme precision with which the crystal structure can be measured, and a second is the constancy of the structural dimensions of the crystal pattern no matter what the origin of the crystal may be nor in what way it may have been treated. For example, measurements of the length of the cubic element of the rocksalt structure made by different investigators on various specimens agree to less than one part in a thousand. Nor does the presence of impurities invalidate the measurements. It is naturally a very great pleasure to the experimenter to find that the crystal responds to every effort that he makes to improve the accuracy of his measurements. And of course it is also gratifying to see in the details of the structures that are revealed, the origins of many of the phenomena which the crystals themselves display, such as the manifold yet invariable details of form, the existence of cleavage and the position of the cleavage plane, the hardness of the diamond, the fibrous appearance of asbestos and so forth. The exactness of the X-ray determinations forms a solid ground on which to found further enquiries.

Yet the very exactness and universality of the X-ray results are evidence of their insufficiency. There are phenomena of the solid state which they cannot of themselves explain. The strength and rigidity of a crystal may vary enormously while there is no change in the X-ray indications and therefore none in the geometric structure of the crystal. There are other properties that display a similar independence in greater or less degree, such as the conductivities for heat and electricity, or the coloration under the action of radiation. Clearly the perfect geometric structure is not the only determining factor in the behaviour of the crystal.

This point of view has been clearly set forth by Smekal: and the promoters of this conference have been gratified by his consent to attend⁹³ and to state his arguments in a comprehensive paper. He has long insisted on a distinction to be drawn between what may be defined as "sensitive" and "insensitive" effects. The latter include all those effects

which are functions of the composition of the crystal itself, and of little else, such as the structure in all its details revealed by X-rays. The former, such as hardness, conductivity and so on may vary widely, being sensitive to external influences and the past history of the crystal. Certain aspects of this question are considered in a very interesting paper by Prof. Ewald and Dr Renninger.

It is perhaps well to pause at this point in order to realize the meaning and purpose of such considerations as these, and of the researches to which they lead. All our investigations of the solid bodies of every form, animal, vegetable and mineral, have as a principal aim the connexion between the properties of the body on the one hand and its composition and architecture on the other. Some of these properties are directly dependent on the few atoms of the unit cell in the crystal. Their arrangement determines the behaviour of the body as a whole. But there are other properties which depend on atomic relations which are not fully developed within the cell: a larger field is required. The action of the atomic forces in groups of hundreds or thousands or tens of thousands of atoms must be considered before we can understand these other phenomena of the Solid State. It is within a region of dimensions covering groups like these that we look for explanations of many matters which affect our ordinary life—the qualities of a steel or a bronze, of a glass or an insulating compound, of a textile fibre or a nerve. And somewhere in this scale of sizes there enters the breath of life to control those atomic compositions which enter into the living organism. We may never learn any more of the life principle than some details of the mechanism which it employs, but it is fascinating to anticipate that it may be possible to know even that little. What then is this condition of a body which so affects its properties and is superimposed upon the geometric crystalline structure? A survey of all properties and behaviours must be made in the attempt to satisfy such an enquiry. For the purpose of this introductory address I need only allude to one such property: the whole field is in other parts well covered by the excellent reports that have been contributed. The cohesive force in rocksalt calculated from a knowledge of its structure and its ionic composition is about 200 kg. per mm². The experimental value varies greatly with the circumstances of measurement but does not usually amount to a single kilogramme. Plastic working of the specimen generally increases the tensile strength in all materials: so does, in the case of rocksalt, handling under water. What is the cause of this immense discrepancy?

This is one striking example of the effect of the unknown factor: we should perhaps say "factors" to cover the possibility that the causes we are looking for are of a complex character.

Other unexplained discrepancies are described and tabulated in the very interesting paper presented by Dr E. Schmid. He shows how in ionic crystals the calculated elasticity constants agree with observations whereas in the case of the metals there is no agreement at all. So also in considerations of slip, plasticity and mechanical twinning there are great divergences to be explained.

A very important question now presents itself: Is this unknown factor or condition directly due to the characteristic properties of the atoms of which the body is composed? Or is it purely the consequence of external and variable influences? Or does the truth lie between these extremes?

Dr Zwicky would answer the question in the first of these three ways. He has sought to prove the existence of a secondary structure within the crystal on a much larger scale than that revealed by X-rays and so regular that it might also be called crystalline. He has tried to show that beside the regular arrangement of positive and negative ions in an ideal crystal there may be other stable arrangements in which the superstructure plays a part. He has also supposed that in their new positions the ions find themselves in electrical fields and are thereby polarised, so adding to the departure from simplicity which the existence of a superstructure requires. These hypotheses have been strongly criticised, notably by Dr Orowan who is contributing a report to this conference. We shall listen to him with great interest. It is a matter of much regret that Dr Zwicky is not here also: but we are to have the pleasure of hearing our President, when he presents an account of experiments due to Dr Goetz, who has been associated with Dr Zwicky in his researches.

In opposition to Dr Zwicky's idea of the regular superstructure naturally associated with each X-ray structure, are those theories which would suppose the unknown condition to be based on the statistical distribution through the material of some sort of irregularities; gaps, flaws, faults, cracks, "Lockerstellen" are some of the descriptive terms. We are fortunate in having here Dr Orowan, Prof. G. I. Taylor and others who have, with great perseverance and brilliant technique developed the theory originated by Griffith that the unexpected weakness of materials is due to cracks, which are particularly liable to lead to rupture if they lie upon the surface. It is a disappointment that Prof. Joffé, who has done so much to clarify our ideas of the strength of materials, is not

here as he had intended, but we welcome some of his distinguished collaborators who will give an account of the work in Leningrad. We are also very glad to have an account by Dr Burgers of those researches in which he connects the history of the treatment of a crystal with its recrystallization properties: since the latter must also be governed by the condition which we are trying to understand, and a knowledge of any of its effects is therefore valuable. 139

On the "accidental" hypothesis the condition determining the peculiar behaviour of solid materials is an irregular distribution of defects which is largely determined by outside influences such as rates of cooling from the melt or formation from solution or cold working, or annealing or the nature of the surrounding medium and so on.

It may appear to some that it is possible to push the "accidental" hypothesis too far. It may seem that the remarkable properties of solid materials which mean so much to us cannot be entirely dependent upon external circumstances: that they must be to some extent connected with the characteristic properties of the different atoms. Otherwise it might be possible to expect a similarity in the behaviour of various materials which would far exceed that which is actually observed, considerable as it is. An excuse for the manifold variety of Nature would be lost.

As matters stand therefore we are aware that there is some highly important condition affecting the properties of the solid over and above the regular arrangement revealed by X-ray analysis. This condition has been the subject of much intensive research: which has tried in the first place to distinguish those properties which are sensitive to this unknown condition from those that are not: which has attempted to determine the nature of the condition, weighing the chances of its being accidental against the possibility of its dependence on atomic properties: which has therefore examined on the one hand with much success the consequences of its consisting in the presence of flaws in the crystalline structure and on the other hand has sought to find direct evidence of a crystalline superstructure by calculation and experimental investigation. There is as yet no general agreement. In some directions definite progress has been made, yet it may be that we are only at the beginning of the search for a solution. We are fortunate in that we can now listen to those who have done so much to obtain the material for that solution, and to draw the proper deductions from what has been observed. iii- i) ii) iii- iv)

A second most important research on phenomena of the Solid State is discussed in the papers of Dr Hückel and Dr Hund who also are here 9, 31

fortunately to speak of their work. This is a more mathematical investigation. As the details of atomic and molecular structure become clearer, more opportunity is provided for the application of mathematical analysis, particularly in its most recent and most powerful forms. Hückel and Hund have taken a prominent part in this development, and their papers are a valuable summary of the progress that has been made. I cannot attempt in this case any preliminary account of this progress, but must leave our visitors to speak for themselves.

The measured dimensions of crystalline structure must serve, if not always as a starting point, at least as a check upon the results of mathematical analysis. They are more useful, the more accurate they are. It is surely very remarkable that in the case of the co-ordinate binding of organic compounds, the centre-to-centre distances of the atoms should be so invariable. A short table by Dr J. M. Robertson gives the results of some of the most accurate measurements that we have, their accuracy depending on the application of Fourier analysis to careful measurements of the absolute intensities of crystal reflection.

I hope that I have done justice in this short introduction to the great importance and interest of those phenomena of the Solid State which are under discussion at this Conference, and I will not longer stand in the way of those who will describe the researches which they have themselves conducted, and will explain to us their significance.

THE STRUCTURE OF MOLECULES AND OF
THE IDEAL LATTICE

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AROMATIC AND UNSATURATED MOLECULES

CONTRIBUTIONS TO THE PROBLEM OF THEIR CONSTITUTION AND PROPERTIES

BY ERICH HÜCKEL
Stuttgart

ABSTRACT. The problems dealt with in this paper arose out of the attempt by the author, some years ago, to give a quantum-theoretical basis to the hypothesis that valency forces in a molecule have a definite direction, and to give a quantum-theoretical interpretation of the binding conditions peculiar to aromatic compounds.

In these cases, the classical theory of valency fails, as is shown for example by the insufficiency of the Kekulé scheme. Again, the peculiar behaviour of the substituted benzenes in chemical reactions shows that the influence of a substituted group extends through the whole of the molecule.

A quantum-mechanical treatment would first calculate the "motion" of the electrons, assuming the nuclei fixed, and then find the equilibrium positions of the latter in the combined field of force. It is, as a rule, both unnecessary and impracticable to carry out the full calculations for aromatic and unsaturated compounds. Indeed, it usually suffices to investigate the motion only of the π -electrons (which have anti-symmetrical eigenfunctions with respect to the plane of the molecule) in the framework of the nuclei and the single bond (σ -) electrons.

The coupling between the π -electrons can be calculated by either of two methods. Method I is essentially the well-known one of Heitler and London. Thus this method approximates to the molecular eigenfunctions solely through a given eigenfunction of the separated atoms.

Reasons are given why method I is not applicable to problems of the nature of those studied in this paper. In particular, it is shown that results calculated by Pauling and his collaborators for the energy contents of the different compounds are in disagreement with experiment.

Method II goes back to Lennard-Jones, Hund and Mulliken. It assigns to each electron in a self-consistent field an eigenfunction which extends throughout the whole molecule. This eigenfunction represents modulated waves. In this method it is found for example that all the bonds in the benzene molecule are equivalent, the conception of single and double bonds having lost its meaning. The characteristic parameter in this method is the resonance integral β . The latter is not independently calculated, but its value deduced from the energy contents of a number of different compounds.

The energy contents of a number of aromatic and unsaturated compounds calculated in this way show on the whole good agreement with experiment.

The problem of free radicles (certain groups with "trivalent" carbon atoms, which can exist in solution) is next discussed. It is evident that the energy of dissociation of the dimer of such a radicle must be less than that due to the breakage of a normal C—C linkage. Nevertheless, it is suggested that the bond does not differ materially in structure from an ordinary one. The small energy of dissociation is due to a gain in resonance energy in the aromatic and unsaturated substituents on dissociation.

The same cause which explains the smallness of the work of dissociation of two aromatic-substituted carbon atoms, also accounts for the smallness of the heat of transformation of diamond into graphite.

In the final section, the peculiar position of the rings containing six π -electrons is considered. Some connexions between constitution and chemical properties are discussed.

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§ 1. INTRODUCTION

THE problem through which I was led some years ago to a theoretical treatment of the compounds referred to in the title was one of more general significance. It was concerned with the question of whether the dominating hypothesis of organic chemistry—that the forces of valency are directed—could be given a meaning in quantum theory. It appeared at first as if the quantum theory of valency as developed at that time, particularly by Heitler and London*, left no room for such directivity, and this problem was receiving little attention from physicists. I therefore searched for a quantum theoretical foundation in a simple case in which there is no doubt about this directivity. The example concerned the stability of cis- and trans-substituted ethylene against rotation round the C=C double bond†. This cannot arise from forces of a classical nature between the substituted groups but must depend on features of the structure of the double bond, amenable to treatment only by quantum theory. By utilizing a method developed by Lennard-Jones‡ for diatomic molecules, and, in particular, his treatment of the oxygen molecule O₂, an explanation of this stability was arrived at§. In ethylene, the pair of electrons which corresponds to the second valency bond has a positional eigenfunction whose nodal plane coincides with that of the molecule, and which is symmetrical in relation to the two carbon atoms (π -linkage of Hund||). The corresponding charge

* W. Heitler and F. London, *Z. f. Phys.* **44**, 455 (1927). F. London, *ibid.* **46**, 455 (1928); **50**, 24 (1928).

† E. Hückel, *Z. f. Phys.* **60**, 423 (1930).

‡ J. E. Lennard-Jones, *Trans. Far. Soc.* **25**, 668 (1929).

§ The electronic structure of ethylene has been recently treated by essentially the same method by R. Mulliken (*Phys. Rev.* **41**, 751 (1932); **43**, 279 (1933)). Also, by another method, by L. Pauling (*Journ. Amer. Chem. Soc.* **53**, 1367 (1931)). See further G. Penney, *Proc. Roy. Soc. A*, **144**, 333 (1934); *Proc. Phys. Soc.* **46**, 333 (1934).

|| F. Hund, *Z. f. Phys.* **73**, 1 (1931); **73**, 565 (1932).

distribution stabilizes the plane arrangement of the atoms. On the other hand the eigenfunction of the remaining electron-pair concerned in the double bond is nearly axially symmetrical about the C=C-axis and has no stabilizing effect (σ -linkage of Hund*).

Another problem through which I was led to a further research on the linkages referred to, was that of the special "aromatic" properties of benzene and related compounds†. This appeared to be connected with the failure of the classical system of valency in these cases, evidenced by the insufficiency of the Kekulé scheme and the many, all more or less unsatisfactory, attempts to establish other valency schemes for the aromatic compounds. Further, there was the peculiar behaviour of the substituted benzenes in chemical reactions‡. This behaviour proves that the influence of a substituted group extends through the whole of the molecule, and indeed in a unique manner which is unknown in the saturated compounds. ("Induced alternating polarities§.")

In the course of these investigations the electronic structures of a number of aromatic and unsaturated substances were treated||. In particular an explanation could be given of the stability of aromatically and unsaturatedly substituted radicals¶. Further, it was found possible to bring some of the chemical properties into line with the electronic structures.

§ 2. GENERAL QUESTIONS RELATING TO THE QUANTUM THEORY OF AROMATIC AND UNSATURATED COMPOUNDS

The quantum-theoretical treatment of molecular structure makes use of the fact that the velocity of motion of the nuclei is small compared with that of the electrons**. One thus proceeds by investigating the electronic structure in terms of the positions of the nuclei, the motion of the nuclei being then treated as taking place in a potential field arising from the system of electrons and nuclei. In the case of polyatomic molecules it is in practice impossible to carry through this treatment in complete generality. However, it is usually sufficient to investigate the electronic structure for such equilibrium configurations of the nuclei as are known to be stable from chemical experience or through the use of physical methods (interference of Röntgen rays or electrons, and spectra). The treatment may be considerably simplified if the arrangement of the nuclei has some symmetrical features.

For the rest, as regards the unsaturated and aromatic compounds, it is quite unnecessary to carry out a complete treatment of the electronic structure, if information is only desired on special features of these compounds. As a rule, though not

* F. Hund, *Z. f. Phys.* **73**, 1 (1931); **73**, 565 (1932).

† E. Hückel, *Z. f. Phys.* **70**, 204 (1931).

‡ Chiefly known from the investigations of A. F. Hollemann, *Rec. Trav. Chim.* 1899-1909.

§ D. Vorländer, particularly *Ber. Dt. Chem. Ges.* **52**, 263 (1919); **58**, 1893 (1925). A. Lapworth, *J. Chem. Soc. London*, **121**, 416 (1922). W. O. Kermak and R. Robinson, *ibid.* **121**, 427 (1922). E. Hückel, *Z. f. Phys.* **72**, 310 (1931).

|| E. Hückel, *Z. f. Phys.* **72**, 310 (1931); **76**, 628 (1932).

¶ E. Hückel, *Z. f. Phys.* **83**, 632 (1933).

** M. Born and R. Oppenheimer, *Ann. d. Phys.* **84**, 457 (1927).

in every case*, it is possible to consider separately those electrons which correspond to one of the two valency bonds comprising a double bond. This results from the following considerations: in the first place it is indicated by chemical experience, and on theoretical grounds it is plausible†, that these electrons are considerably more loosely bound than are those which are to be assigned to single bonds and to the first bond of a double bond (σ -electrons). In the second place, to these electrons are assigned eigenfunctions which, in the case of the plane arrangement usual for unsaturated and aromatic linkages, have a symmetry different from that of the σ -electrons. The latter are in fact symmetrical, and the former anti-symmetrical in relation to the plane of the nuclei. We call the electrons with anti-symmetrical eigenfunctions, π -electrons. The first consideration indicates that a variation in the configuration of the π -electrons as a result of Coulomb forces and polarization, will have small effect on that of the σ -electrons; and the second shows that the resonance action between the two classes of electrons vanishes‡. It is therefore usually sufficient to deal exclusively with the π -electrons—only such cases have so far been dealt with. We thus investigate the distribution of these electrons in the “framework” of the molecule, which may be considered as consisting of the nuclei and a fixed distribution of charge due to the σ -electrons.

According to chemical evidence the molecule of benzene is plane and has a six-fold symmetry. This is at least not in conflict with the results of X-ray and electron-ray analysis§. On this account we consider the π -electrons as being in a framework with this kind of symmetry. Each carbon atom provides three electrons in the L -level for the three single valency bonds which radiate from it, so that, together with the electrons in the hydrogen atoms, an electron-pair can be assigned to each single bond. We shall not discuss fully here the way in which this arrangement is to be described according to wave mechanics. The essential points are that these electrons form a complete system in the sense of Pauli's principle, and that they have eigenfunctions which are symmetrical with respect to the plane of the ring. Each carbon atom still has one remaining L -electron, whose eigenfunction has a node in the plane of the ring, and which we name a π -electron. Figure 1 shows qualitatively the charge distribution which is associated with such a π -electron (arbitrary units).

We have now to consider the coupling between these π -electrons. I have already carried out this investigation in my first paper concerning the benzene molecule, using two methods||:

* As an example of a system of atoms in which this is not the case we may consider the radicle $(C_6H_5)_3C-C(C_6H_5)_2$, in which, for the accepted space arrangement of the atoms, a resonance action is possible, for reasons of symmetry, between the σ -electrons in the tetravalent carbon atom and the π -electrons of the remaining carbon atoms. This is probably connected with the marked stability of this radicle.

† F. Hund, *Z. f. Phys.* 73, 1, 457 (1931); 73, 565 (1931). ‡ Cf. note *, above.

§ In the interpretation of the Raman spectrum of benzene, however, the acceptance of this kind of symmetry leads to difficulties. (G. Placzek, *Leipziger Vorträge*, Hirzel, 1931, p. 100.) Since there is no evidence for any other definite structure, we thus adhere to the plane arrangement and six-fold symmetry.

|| Both methods were previously employed by Bloch for the treatment of the forces between electrons in crystal lattices. F. Bloch, *Z. f. Phys.* 52, 555 (1928); 61, 206 (1930).

Electron pairs I. The method of Heitler and London (Method I).

val? orbitals II. The method of Lennard-Jones, Hund and Mulliken (Method II).

§ 3. METHOD I

The first method was carried through following a mathematical treatment of Slater*. Pauling† has since used an essentially simpler mathematical procedure, which goes back to Weyl and Rumer‡, for calculating the states of least resultant total spin s (in this case $s = 0$) to which the fundamental state always belongs. This

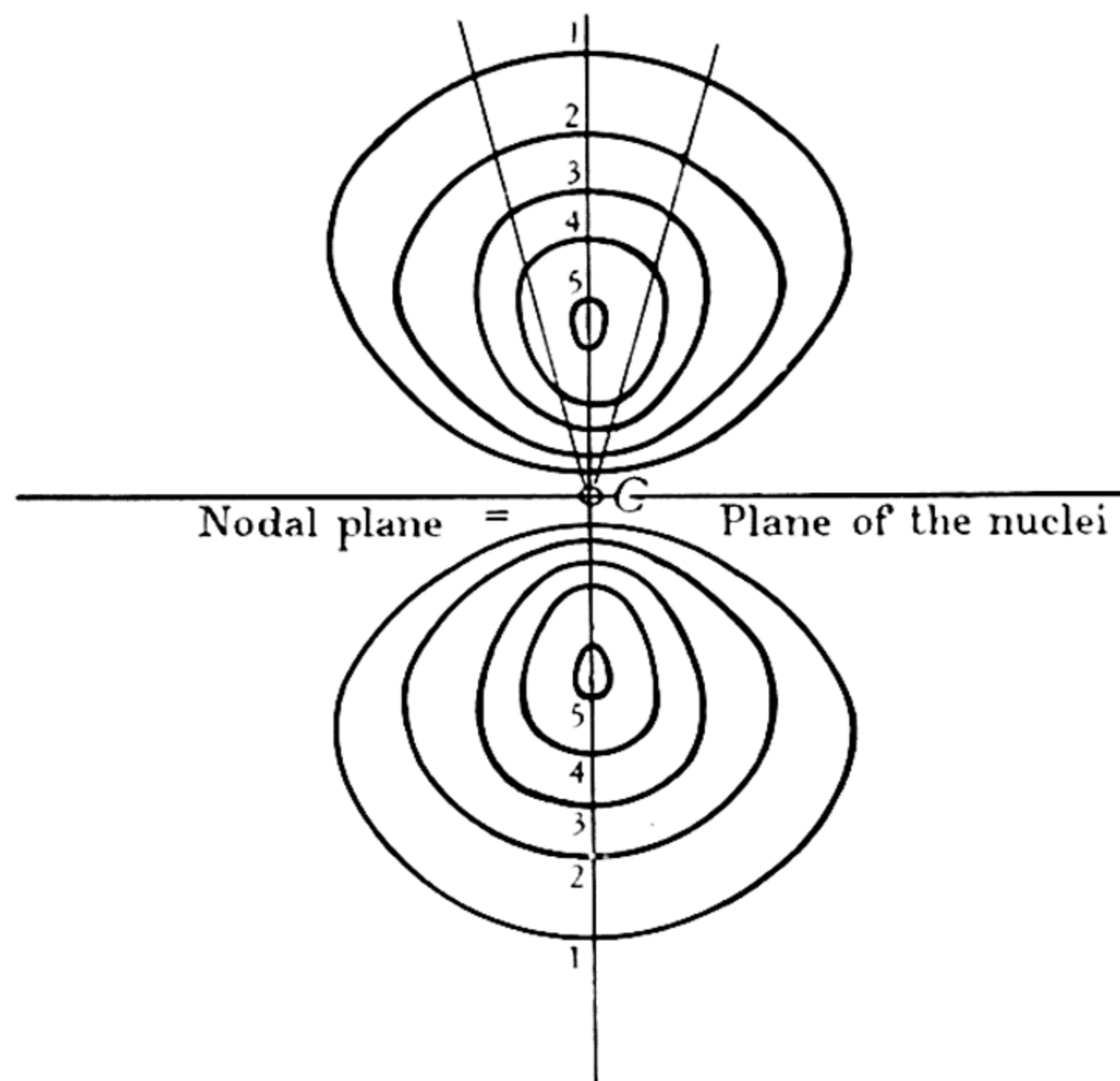


Figure 1. Curves of constant charge density in a plane through a C-nucleus, perpendicular to the plane of the nuclei.

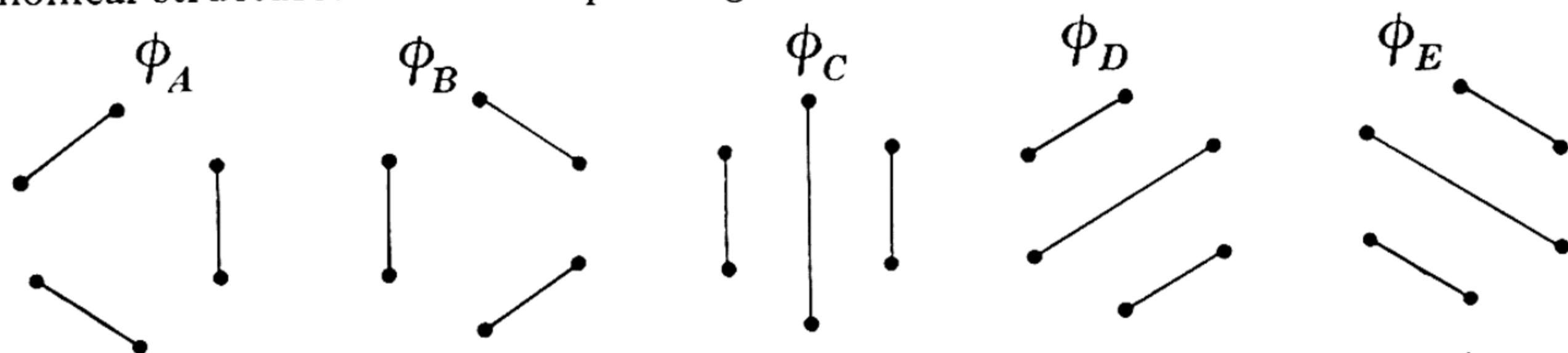
method, however, differs from the earlier one only in the mathematical treatment, and thus leads to the same results. Method I commences, as regards the coupling referred to above, by assigning to each carbon atom a π -electron which is in a given state with the positional eigenfunction $\phi_a(r_{ia})$ (the suffixes indicating the i th electron in the atom a). The total positional eigenfunction, taking coupling into account, is written as a linear combination of the products $\phi_1(r_{i1}) \dots \phi_6(r_{i6})$, and, starting from this, the Heitler-London perturbation method is worked out (to the first approximation). Of course, only such linear combinations are considered as satisfy the Pauli principle when the spin is allowed for. (Coupling between spin and orbit, as well as between the spins themselves, is neglected.) The Rumer-Pauling method now proceeds by selecting from these linear combinations those which correspond to the smallest value of the total spin (in this case $s = 0$), and choosing from these, in a certain way, the ones which are linearly independent. These functions which belong to the value $s = 0$, can be associated with models

* F. C. Slater, *Phys. Rev.* **34**, 1293 (1929); **35**, 511 (1930).

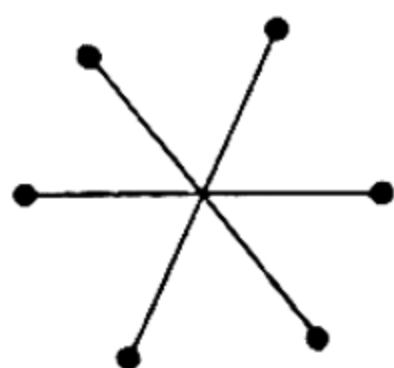
† L. Pauling, *J. Chem. Phys.* **1**, 280 (1933). L. Pauling and G. W. Wheland, *ibid.* **1**, 362 (1933).

‡ H. Weyl, *Nachr. der Ges. der Wiss., M.-Ph. Klasse*, p. 285 (1930); p. 33 (1931). G. Rumer, *ibid.* p. 337 (1932). G. Rumer, E. Teller and H. Weyl, *ibid.* p. 499 (1932).

of the valency pattern (of the π -electrons) in which the atoms are joined in pairs by single bonds, one and only one bond radiating from each atom in such a way that the bonds do not cross one another*. The schemes of valencies corresponding to the functions so chosen are called by Pauling "canonical structures." The problem of secular perturbations corresponding to these functions may be formulated and solved by a method due to Rumer and Pauling for the case where attention is confined to coupling between adjacent atoms. In the case of benzene there are five canonical structures with corresponding "canonical functions":



A and B correspond to the Kekulé forms, C , D and E to the Dewar forms. To every other structure, for example that of Claus:



there is a corresponding linear combination of the canonical functions,

$$\phi_{\text{Claus}} = \phi_A + \phi_B - [\phi_C + \phi_D + \phi_E].$$

The canonical functions are not "eigenfunctions"; in other words, they do not represent states of definite energy. In fact, to the states of definite energy there correspond linear combinations of the canonical functions which, with the corresponding eigenvalues, are determined from the perturbation problem. Denoting by J_0 the Coulomb integral and by J ($J < 0$) the exchange integral of the theory of Heitler and London, each for the π -electrons of two adjacent atoms, then the solution of the perturbation problem gives for the coupling energy and the eigenfunction of the π -electrons in the ground state of benzene the expressions

$$6J_0 + (\sqrt{13} - 1)J = 6J_0 + 2.6055J;$$

and

$$\phi = 0.62435(\phi_A + \phi_B) + 0.27101(\phi_C + \phi_D + \phi_E).$$

Thus, in the sense of the method of approximation employed, the ground state may be considered as resulting from the superposition of the two Kekulé and the three Dewar forms. The ground state possesses six-fold symmetry, in agreement with chemical evidence.

For illustration, the total coupling energy of the ground state may be split up. For a Kekulé system by itself the "exchange energy" (e.e.) would have the value $\frac{3}{2}J$ and for a Dewar system the value 0. The difference between the actual e.e. and that for a Kekulé system alone ($1.1055J$) may be referred to as the "resonance energy"

* In general crossing cannot take place if the atoms—independently of their actual configuration in space—are regarded as being arranged on a circle.

(r.e.) of the structure (taken in relation to a Kekulé system). This again may be regarded as split up into a reciprocal r.e. of the two Kekulé structures and a remainder (the first fraction has the value $0.9J$ and the second $0.2055J$).

Pauling and his co-workers* have applied method I to a whole series of aromatic and unsaturated compounds, and, among other applications, have employed it for treating free radicles with aromatic substituents for whose stability they gave an explanation. They have further discussed the connexion between the results and the energy content of the substances. In contrast to this I considered as early as my first work on benzene, that I had been able to show that method I was unsuitable for handling the coupling of the π -electrons, since it appeared that this method leads to results which are not in agreement with experiment. cf. 32

Method I confines itself to the first approximation of the Heitler-London theory. Thus in the first place the objections which may be brought against the application of the method from a purely theoretical standpoint, are the same as may be raised generally against the applicability of this approximation. The method approximates to the eigenfunctions in the molecule solely through a given eigenfunction of the separate atoms, while in reality, the eigenfunctions of the higher states of the separate atoms are more or less involved in the molecular functions. This may also be expressed as a neglect of the capacity for polarization which must be taken into account in the next approximation of the Heitler-London theory. Also, no attention is given to the possibility that in a single atom there may be two electrons in the same state ("polar states" of Slater). It is very difficult to estimate in a given case to what extent the quantitative results will be affected by the neglect of these considerations. On the other hand the principal advantage of method I is that its formal scheme goes far to provide a picture of the arrangement of the valencies and shows how the classical scheme of valencies, which fails here, may be extended so that a state may be considered as arising from the superposition of different valency patterns. However, this advantage is naturally not sufficient if the quantitative results cannot be brought into agreement with experience, whereas as we shall see this will be the case for the results of method II. The failure of method I is shown by the following considerations:

(1) Method I leads to results for the energy content of aromatic and unsaturated compounds which are not in agreement with experiment. (This is established here for the first time.)

(2) It fails to indicate the distinctive nature of rings with six π -electrons.

(3) For substituted benzenes, there follows from it a disturbance of the charge distribution in the molecule, resulting from the substitutions which cannot be brought into correspondence with the reactive properties of the substituted benzene.

We shall consider below the evidence on which these assertions are based.

Concerning 1. Method I always gives a smaller absolute value for the c.e. per π -electron in conjugated and aromatic systems, i.e. a smaller binding energy (larger

* L. Pauling and G. W. Wheland, *J. Chem. Phys.* 1, 362 (1933). L. Pauling and J. Sherman, *ibid.* 1, 606 (1933); 1, 679 (1933). [Note added in proof: See also G. W. Wheland, *ibid.* 2, 474 (1934); J. Sherman, *ibid.* 2, 488 (1934).]

energy content), than in an isolated double bond. In contradistinction to this it is known that the binding energy is always greater (i.e. the energy content is smaller) for conjugated and aromatic systems than the value which would be calculated from the isolated double bonds. For example, the e.e. of benzene according to method I is $2.6055J$, and the e.e. for three isolated double bonds amounts to $3J$. Thus according to this benzene would have a smaller binding energy than would be associated with three isolated double bonds. The observed binding energy is, however, greater. Pauling and Sherman give the energy content (negative binding energy) as $E = -58.20$ e.V. (observed) and $E' = -56.58$ e.V. (estimated for three separate double bonds)*. Nevertheless these authors come to the conclusion that the result of method I is in agreement with experiment. This claim, however, is based on an erroneous method of calculation. The authors in fact set the difference $E - E'$ equal to the resonance energy referred to a Kekulé structure:

$$E - E' = -1.62 \text{ e.V.} = 1.1055J,$$

and so obtain $J = -1.5$ e.V. It is not, however, permissible to set these two quantities equal to one another. For E' is calculated with the binding constant of an isolated double bond; $E' = 3.(C-C) + 3.(C=C) + 6.(C-H)$, and three isolated double bonds have the value $3J$ for the e.e. In contradistinction to this the Kekulé structure, to which the r.e. refers, has an e.e. equal only to $\frac{3}{2}J$.

Denoting by E' and E the calculated and observed energy contents (negative binding energies) respectively we may write

$$\begin{aligned} E' &= E_0 + 3J, \\ E &= E_0 + \frac{3}{2}J + 1.1055J, \end{aligned}$$

where E_0 has the same value in both equations and denotes the energy content apart from the exchange energy, since, of course, E' and E should only differ from each other as a result of the different value of the e.e. for three isolated double bonds and for the benzene structure respectively. (Pauling and Sherman's argument implies the incorrect statement $E' = E_0 + \frac{3}{2}J$.) Then follows

$$E - E' = -1.62 \text{ e.V.} = (1.1055 - \frac{3}{2})J,$$

so that $J > 0$ (repulsion instead of attraction!) and *not* as according to Pauling and Sherman

$$E - E' = -1.62 \text{ e.V.} = 1.1055J.$$

In a similar way all the calculations of Pauling and Sherman are in error†, wherever the differences between the values E' calculated from the binding constants and the actual values E have been identified with the resonance energies deduced from quantum theory.

The results of method I are therefore not in agreement with experiment as regards

* These binding energies, unlike those usually adopted, are referred to a separation into C-atoms which are in a state 1 e.V. higher than the normal, instead of to the latter condition itself. (It was at that time assumed that separation resulted in C-atoms in the 5S state, and that this lay 1 e.V. above the ground state. Although we now know that the latter is not true, we can use the values given above, since only their differences occur here, and these are independent of which state of the free C-atom is used as standard for the binding energies.) 1 e.V. = 23.054 k. cal./mol.

† Note added in proof: The same holds for the recent work of G. W. Wheland, *J. Chem. Phys.* 2, 474 (1934).

the energy content. But it is worthy of note that for various compounds the *differences* between the resonance energies calculated by Pauling and Sherman for the different compounds in general coincide quite well with the *differences* in the values of $E - E'$ calculated by their method.

Concerning 2. Method I is unable to explain why rings containing six π -electrons possess a remarkably stable configuration of electrons; nor why although the five-ring enters as an ion into such combinations as $[\text{C}_5\text{H}_5]^- \text{K}^+$, yet no compounds such as $[\text{C}_7\text{H}_7]^- \text{K}^+$ are known. Further, why hetero-cyclic rings with five atoms, such as pyrrole $(\text{CH})_4\text{NH}$, to which six π -electrons must be attributed, are fairly similar in their chemical properties to the aromatic compounds. That the symmetrical arrangement of the valencies at angles of 120° cannot be entirely responsible for this, but rather that it depends on the number, six, of the π -electrons, is shown most clearly by the existence of metallic compounds of $[\text{C}_5\text{H}_5]^-$ and the non-existence of such compounds of $[\text{C}_7\text{H}_7]^-$ *. For the five-ring itself, C_5H_5 , method I leads to a very small e.e.: $1.23607J$. The seven-ring has not been calculated. The ions are not amenable to treatment by this method.

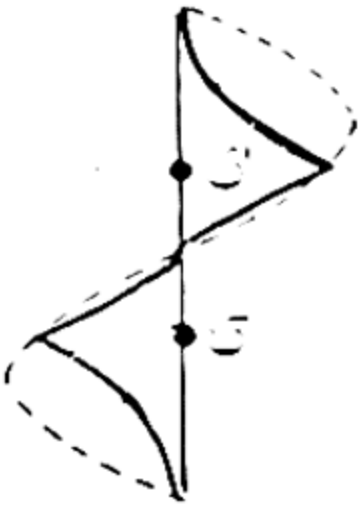




Concerning 3. In the case of reactions with substituted benzenes (for example, the nitration of toluene) it is known that the different possible reaction products (*o*-, *m*-, *p*-nitrotoluene, $\text{C}_6\text{H}_4\text{CH}_3\text{NO}_2$) are not produced to the same extent (a "directive action" of the substituent). The differences of the heats of activation Q for the example mentioned are, in k. cal./mol.:

$$Q_o - Q_p = 135, \quad Q_m - Q_o = 1490, \quad Q_m - Q_p = 1625,$$

while the activity constants A are approximately equal†. The principal products are then the *o*- and *p*-, and only to a small extent the *m*-compound. If instead of the "negative" substituent CH_3 we have a "positive" one, for example COOH , the relations are reversed. In the nitration of benzoic acid, for instance, $Q_m - Q_o = -800$ and Q_p is so large that the *p*-compound is usually not produced in a measurable quantity. This shows that the different heats of activation are determined by the character of the substituted group, the influence of which extends through the whole molecule ("induced polarities"). Since this kind of action is not known in the case of unsaturated compounds, the different heats of activation for the *o*-, *m*- and *p*-compounds must be determined by the disturbance of the configuration of the π -electrons by the substituent. The relative magnitudes of the alterations in the charge density of these electrons in the *o*-, *m*- and *p*-atoms can be calculated from the electronic structure of the ground state and the excited states of the π -electrons. In this way from the states determined by method I, we obtain modifications of the charge distribution which are equal in the *o*- and *m*- and less in the *p*-form. According to method II, on the other hand, we obtain ratios for these disturbances which are in step with the heats of activation of the different forms. The reason is,

* As regards the significance of the number 6 of "double bond (π) electrons" in the 5-rings, see the discussion by W. Hückel, *Theoretische Grundlagen der organischen Chemie*, 2nd edition, 1, 386 et seq. (1934).

† A and Q are defined by the formula of Arrhenius $K = Ae^{-Q/RT}$ for the constant K of the reaction velocity.

Eigenfunctions	Resonance energies	Term spectrum	Ground state
			• Mean resonance energies
 <p>1. Overtone</p>	$+\beta$	$-\frac{1}{2} \beta$	$-\frac{1}{2} \beta$
 <p>Fundamental</p>	$-\beta$	0	0
Isolated double bond			
 <p>2. Overtone</p>	$+\sqrt{2} \beta$	$-\frac{1}{2} \beta$	$-\frac{1}{2} \beta$
 <p>1. Overtone</p>	0	0	0
 <p>Fundamental</p>	$-\sqrt{2} \beta$	$-\frac{1}{2} \beta$	$-\frac{1}{2} \beta$
			• -0.91β
			$-\frac{1}{2} \beta$
			Radicle

that in method I only some of the excited states are obtained, while the polar states of Slater are not considered.

§ 4. METHOD II

In method II (which Mulliken calls the method of "molecular orbitals") to each electron is assigned an eigenfunction which extends through the whole of the molecule. These, and the associated eigenvalues are to be conceived as in a "self-consistent" (Hartree) field which arises from the charge of the nuclei and the statistical charge distribution of all the electrons apart from the one directly under consideration. In this case also, the π -electrons may be considered separately, since in the different compounds, the charge distribution of the other electrons in a carbon atom and the distances of separation of the nuclei are treated as independent of the coupling of the π -electrons to the first approximation. The method proceeds by first taking the Hartree field as being independent of the state in which a single electron is considered to be. This Hartree field may be represented as a superposition of the Hartree fields V_f associated with the individual atoms

$$V(r) = \sum_f V_f(\mathbf{r} - \mathbf{R}_f) \quad \text{.....(1)}$$

(f is a number identifying the particular atom, \mathbf{r} the position vector of an electron and \mathbf{R}_f that of the f th C-nucleus).

At the same time V_f is taken to have the same value for all the atoms*.

Denoting then by $\psi_f^{(0)}$ the eigenfunction corresponding to the lowest eigenvalue $W^{(0)}$ of a π -electron in the field V_f , the eigenvalues and eigenfunctions in the field V are written as

$$W^{(k)} = W^{(0)} + \Delta W^{(k)} \quad \chi^{(k)} = \sum_f a_f^{(k)} \psi_f^{(0)}(\mathbf{r} - \mathbf{R}_f) \quad \text{.....(2)}.$$

The $\Delta W^{(k)}$ and the corresponding set of coefficients $a_f^{(k)}$ are then determined from a problem of secular perturbations. If the coupling between adjacent atoms only is considered, and if the non-orthogonality of the eigenfunctions of adjacent atoms is neglected, $\Delta W^{(k)}$ always has the form

$$\Delta W^{(k)} = -\alpha + b \cdot \beta \quad \text{.....(3)}.$$

Here α is the "Coulomb integral"

$$\alpha = -\frac{1}{2} \int (\psi_1^{(0)2} V_1 + \psi_2^{(0)2} V_2) d\tau > 0 \quad \text{.....(3a)},$$

and β is the "resonance integral"

$$\beta = -\frac{1}{2} \int \psi_1^{(0)} \psi_2^{(0)} (V_1 + V_2) d\tau > 0 \quad \text{.....(3b)}$$

(1 and 2 being adjacent atoms); b is a numerical factor. The functions $\chi^{(k)}$ represent modulated waves. The course of these functions along the chain of carbon atoms is shown qualitatively in figure 2, for the isolated double bond and the systems as involved in



* The values of V_f could also, of course, be considered as being different: for example we should strictly distinguish between V_f for such carbon atoms as have three other carbon atoms adjacent to them, and for those having two or only one (as, for example, in naphthalene or at the ends of a chain).

(The functions have opposite values above and below the plane of the molecule.) We always obtain as many states as there are C-atoms present. States in which $b < 0$ are binding, while those with $b > 0$ are loosening owing to the resonance. The ground state is arrived at by filling up the $\chi^{(k)}$'s in order of increasing energy, so that each state is not occupied more than twice. The total energy of coupling is equal, in the sense of Hartree's method, to the sum of the coupling energies for the occupied $\chi^{(k)}$ states.

In this connexion, states with negative values of b contribute to binding and states with positive values of b to a loosening of the atoms. A state which has no nodes between two atoms leads to an attraction while one which has a node there leads to a repulsion between the two atoms. In conjugated systems the bonds cannot be localized or can only be partially localized. So for example in the ground state of butadiene two of the occupied states link all four carbon atoms. The two other states link the outermost atoms C_1, C_2 and C_3, C_4 , but loosen C_2, C_3 . Corresponding to this the central binding is weaker, but is nevertheless not an ordinary single bond. Since the charge density of the π -electrons is relatively small there, this linkage will be less stable against rotation than a double bond. This applies in a corresponding way to the binding between the central carbon atoms in diphenyl. The result is in agreement with chemical evidence, according to which there is no rigidity against rotation between the atoms C_2 and C_3 . Nevertheless we have to admit that for these linkages also the plane arrangement is the most stable. (It may be, however, that a non-plane arrangement is forced to be stable by voluminous substituted groups; compare for instance the o - and o' -derivatives of diphenyl.) It is especially in benzene that all the bonds are equivalent. The representation with double and single bonds loses its meaning in this case.

In figure 2 the resonance energies are also shown. The Coulomb action is always proportional to the number of carbon atoms. In the figure ---|---| denotes a state which can be occupied twice (not degenerate), ---|---| such a state doubly occupied, and ---|---| such a state singly occupied. The point \bullet indicates the mean resonance energy per π -electron. (Term centre for the occupied states.)

In criticism of method II the following is worthy of note. The method appears at first to neglect the exchange action between the electrons, and in fact the Hartree method as normally used also has this feature. It may be shown, however, that for the ground state, where either all the occupied states are occupied in pairs, or all in pairs except one, the exchange is largely taken into account if by the expression $V_f(\mathbf{r} - \mathbf{R}_f)$ in (1) we understand the following sum*:

$$V_f = V_f^0 + \frac{1}{2}v_f \quad \dots\dots(4),$$

* The method of proof of the theorem used here corresponds to the treatment given by Fock (V. Fock, *Z. f. Phys.* 61, 126 (1930), T. Koopmanns, *Physica*, 1, 104 (1934)). Fock's equations may be written (in Hartree units)

$$\left[H(\mathbf{r}) + \sum_k \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{kk} - W^{(i)} \right] \chi^{(i)}(q) = \sum_k \chi^{(k)}(q) \cdot \left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{ki},$$

where q denotes x, y, z and the spin components σ_i in a given direction. $\left(\frac{1}{|\mathbf{r} - \mathbf{r}'|} \right)_{ki}$ are the matrix

where V_f^0 is the potential which arises from the nucleus and the σ -electrons of the f th atom; v_f is the potential arising from the charge distribution $\psi_f^{(0)2}$ itself:

$$v_f = \int \frac{\psi_f^{(0)2}(\mathbf{r}' - \mathbf{R}_f) e^2}{|\mathbf{r} - \mathbf{r}'|} d\tau' \quad \dots\dots(4a);$$

and $\psi_f^{(0)}$ is the lowest eigenvalue of the eigenfunctions belonging to the Schrödinger equation

$$\left\{ \Delta + \frac{8\pi^2 m}{h^2} [W - V_f(\mathbf{r} - \mathbf{R}_f)] \right\} \psi_f(\mathbf{r} - \mathbf{R}_f) = 0 \quad \dots\dots(4b).$$

In order that the exchange may be largely allowed for it is always essential that the influence of $\frac{1}{2}v_f$ on the resonance energy should be small compared with that of $V_f^{(0)}$. It is then also permissible to regard the Hartree field $\sum_f V_f$ as being approximately the same for all the $\chi^{(k)}$ -states. This hypothesis may be realized. We may also further assume for molecules with a larger number of π -electrons that in cases where only two states are not doubly occupied, the exchange is sufficiently accounted for by (4).

Method II, in contrast to I, takes account of the polar states. It is, however, not correct to say, without further proof, that the method gives far too great consideration to these states. This would only be correct without doubt if the eigenfunctions in the field V_f^0 (and not in V_f) were used for the approximation, with simultaneous neglect of the exchange. After all it cannot be stated without further examination how large are the errors which arise from the fact that only linear combinations of functions of the form $\chi^{(1)}(r_{i1}) \dots \chi^{(n)}(r_{in})^*$ are permitted as solutions of the complete Schrödinger equation.

If we give preference to method II over method I, notwithstanding the uncertainties from the theoretical standpoint as to how far the two methods represent an approximation to the truth, the reason is that it has been shown that method II represents largely the facts of experiment, and particularly in cases where method I has been proved to be inadequate. We grant that this state of affairs is unsatisfactory from a purely theoretical standpoint. Considering, however, the great difficulties which present themselves in a quantitative estimation of the limits of accuracy, it appears scarcely possible to renounce the heuristic point of view.

elements of $\frac{1}{|\mathbf{r} - \mathbf{r}'|}$ in the system of the $\chi^{(k)}(q)$. The summation extends over all the occupied states. Finally, we have $H(r) = -\frac{\Delta}{2} + \sum_f V_f^{(0)}(\mathbf{r} - \mathbf{R}_f)$. From this and from the equation

$$\chi^{(i)}(r) = \sum_f a_f^{(i)} \psi_f^{(0)}(\mathbf{r} - \mathbf{R}_f)$$

the result given above follows if the terms which involve the products $\psi_f^{(0)}\psi_{f+1}^{(0)}$; $\psi_f^{(0)}\psi_{f+2}^{(0)}$ are neglected as being small compared with the terms involving $\psi_f^{(0)2}$. If neglect of these terms is to be permissible it is essential that the influence of $\frac{1}{2}v_f$ on the resonance action shall be small compared with that of $\Delta_f^{(0)}$.

* Cf. R. S. Mulliken, *Phys. Rev.* 41, 68 et seq. (1932).

§ 5. RESULTS AND DISCUSSION OF METHOD II

Consequently we confine ourselves below to the results of method II, and to the discussion of the conclusions which can be drawn from these results as regards the constitution and properties of the compounds dealt with here.

(a) *Energy contents*

We obtain, in the first place, information on the relative energy contents of different aromatic and unsaturated compounds, and indeed (unlike that furnished by method I) it is not in qualitative disagreement with experience. Table 1 gives a survey of the resonance energies as multiples of β for a series of compounds. It should be noted that in the calculation, the same V_i has been ascribed to every C-atom: for example in naphthalene all the C-atoms are considered as equivalent. Since it is difficult to express the deviations for the different C-atoms, we have hitherto not attempted to take account of these differences.

A part of the data of table 1 is set out in figure 3. In this, a black spot ● represents the mean energy of binding per π -electron in the ground state of the molecule. We shall later with the aid of this figure discuss some correlations between electron structure and properties.

The resonance integral β is the characteristic magnitude of the theory. To calculate its value theoretically would be exceedingly difficult. On the other hand, we can derive its value from the observed energy content of different aromatic and unsaturated compounds. Thus from the energy content $E = -58.20$ e.V., and the value $E' = -56.58$ e.V. calculated (see p. 16) from the binding constants (for three separate double bonds), we have, from the relations

$$E = E_0 - 8\beta; \quad E' = E_0 - 6\beta,$$

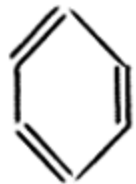
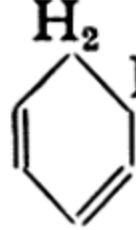
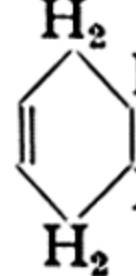
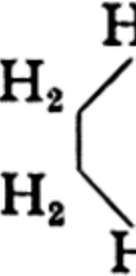
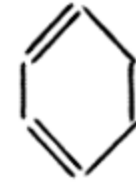
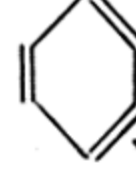
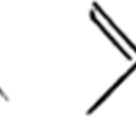
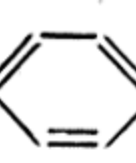
the equation
$$\beta = \frac{E' - E}{2} = 0.81 \text{ e.V.} = 18.7 \text{ k. cal./mol.}$$

However, the calculation of β by means of the binding constants is not wholly free from doubt, since the binding constants contain a certain arbitrariness. This arbitrariness arises mainly because the binding constants of the C—H bond in aliphatic, unsaturated and aromatic compounds have been assumed the same. Elsewhere, I have shown* how the value of β can be determined from the heats of hydrogenation in the case of benzenes having different heats of hydrogenation, without using the binding constants. This method of calculation involves only the assumption that the structure of the σ -bond is not changed by the resonance effect of the π -electrons, and that the magnitudes α , β can be assumed equal for all C-atoms with a π -electron. It agrees therefore with the assumptions and simplifications (cf. p. 20) underlying the theory. By the method stated, the result found is $\beta = 15$ k. cal./mol. The uncertainty of this value is due to the inaccuracy with which the heats of hydrogenation are known. On this account, and since the use of the binding constants cannot generally be avoided in this way, exact calculation of the energy contents is not possible. Nevertheless using the binding constants

* E. Hückel, *Z. f. Phys.* 83, 665 (1933).

we find on the whole that the energy contents of aromatic and unsaturated agree fairly well with the theory, using the approximate value $\beta = 20$. Table 2 contains a short list of some compounds from which this may be seen. If E is the observed and E' the energy content*, calculated from the binding constants of just so many $C=C$ bonds as the molecule contains double bonds, then $E' - E$ is interpreted as the difference between the resonance energy $- 2x\beta$ for x separate bonds, and the

Table 2. Energy contents

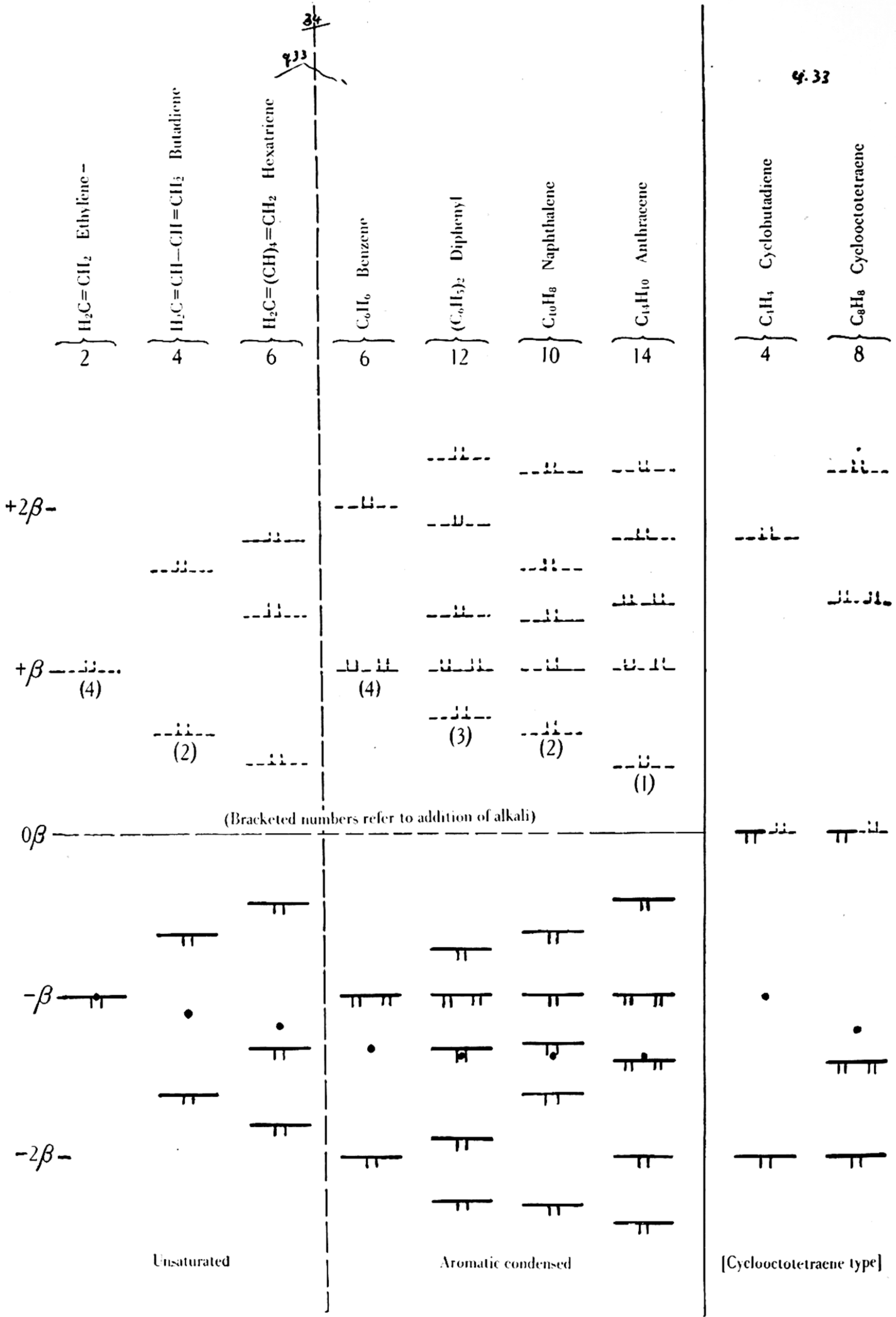
Compounds (formulated with double bonds)	$-E$, where E is observed energy content k. cal./mol.	$-E'$, where E' is energy content calculated from binding constants k. cal./mol.	$E' - E$ k. cal./mol.	$x\beta$ theoretical	$x\beta$ for $\beta = 15$ k. cal./mol.	$x\beta$ for $\beta = 20$ k. cal./mol.	$\frac{E' - E}{x} = \beta$ k. cal./mol.
 Benzene	1202	1165	37	2β	30	40	18.7
 1, 2 dihydrobenzene	1306.5	1298	8.5	0.48β	6.7	9.6	17.7
 1, 2, 3, 4 tetrahydrobenzene	1424.5	1430	5.5	0β	0	0	—
 Cyclohexane	1547	1562	15	0β	0	0	—
 Naphthalene	1904	1828	76	3.68β	55	74	20.6
 Anthracene	2595	2490	105	5.314β	80	106	19.7
 Diphenyl	2305	2217	88	4.383β	66	88	20
 Stilbene	2701	2606	95	4.878β	73	97	19.5

The values of the binding constants used (from Pauling and Sherman, calculated for the C-atom in the ground state) are $(C-H) = 93.9$, $(C-C) = 72.6$ and $(C=C) = 128.3$.

cf. 22

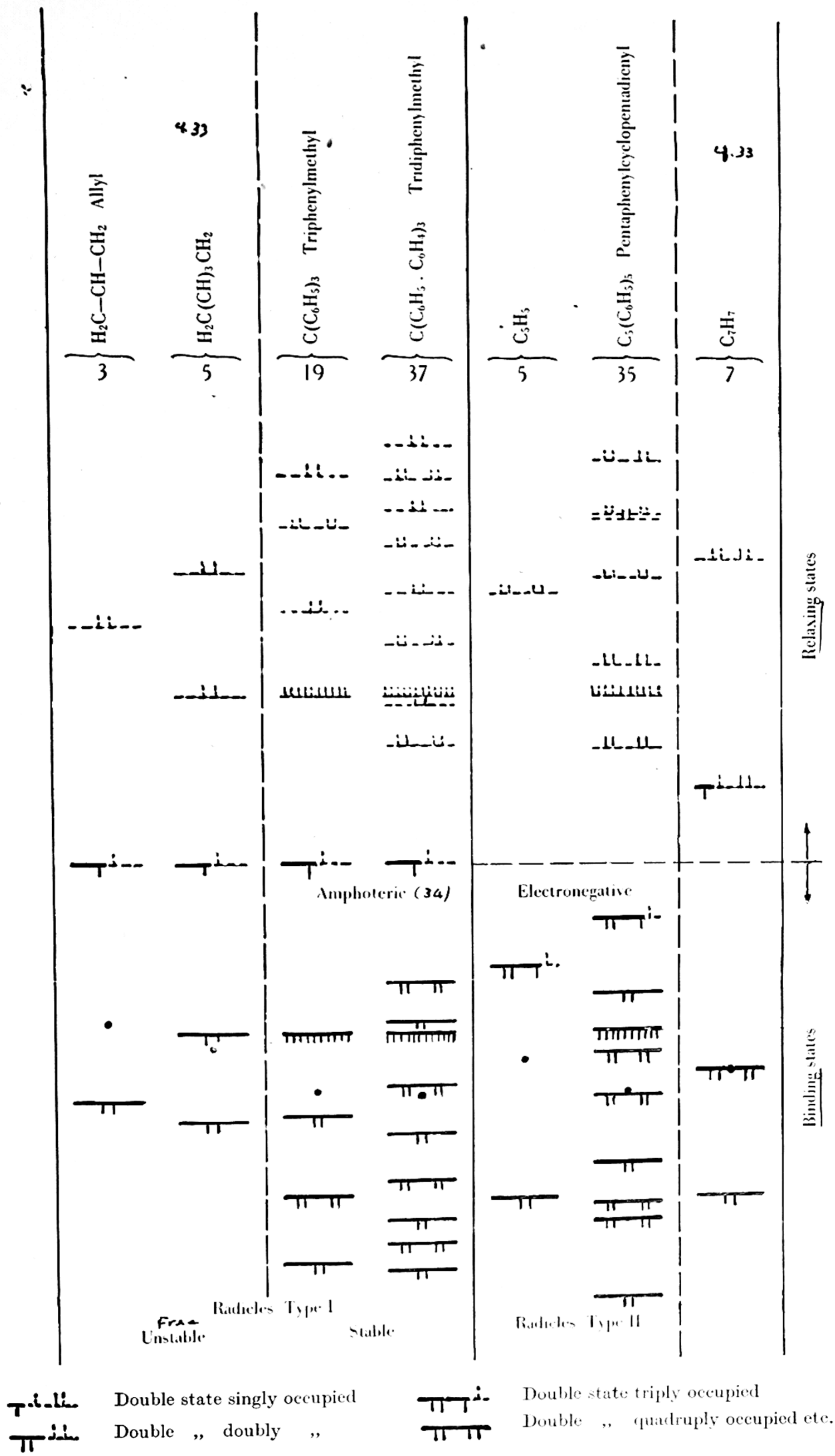
true resonance energy. If this is > 0 it means that the resonance effect gives a smaller energy content than has been calculated for the corresponding number of separate double bonds. It is obtained theoretically from the results given in table 1 as a multiple of β , viz. $x\beta$.

* In part these have been taken from the work of Pauling and his collaborators, but they are calculated here for the C-atom in the normal state. (Cf. p. 16, f.n.) Here therefore E' is as many electron volts less than Pauling's figures as there are C-atoms in the molecule, and the binding constants are less by $\frac{1}{4}$ for $C-H$, by $\frac{1}{2}$ for $C-C$ and by 1 e.V. for $C=C$.



Single state unoccupied Single state doubly occupied
Single „ singly occupied Double „ unoccupied

Figure 3 1.23



It will be seen that in contrast to the results of method I, $E' - E$ always comes out > 0 , in harmony with observation. In table 2 the values of $\alpha\beta$ are given, which are obtained with $\beta = 15$ or 20 k. cal./mol. respectively. The last two columns show that the values of $(E' - E)$ are closely proportional to α , and that with $\beta = 20$, we obtain satisfactory calculated values of $E' - E$ and therefore of the actual energy content E . Naturally it is to be noted that the calculation by means of the binding constants entails some uncertainty (see for example cyclohexane, where $E' - E = 15$ k. cal./mol., whilst $E' - E$ should be zero). On the whole we can, however, conclude that method II gives results for the energy content which agree with the observations as well as can be expected from the basis underlying the calculations.

(b) Free radicles

In general free radicles with "trivalent" C are not stable substances even if their individual molecules represent stable atomic arrangements. The reason for this is that by coalescence of two such radicle molecules, a chemical compound is produced which is formed with a large gain in free energy. This increase is in most cases of the order of the binding constant of a C—C linkage, and is therefore about 70 k. cal./mol.

There are, however (in solutions), certain radicles with "trivalent" C, which exist as stable substances or in a measurable dissociation equilibrium with their dimers. In every case where this is known, aromatic or unsaturated substituents are attached to the "trivalent" C-atom. In these radicles, the increase of free energy in dissociation of the dimers must be much smaller than for a normal C—C linkage. In fact Ziegler and Ewald* found the heat of dissociation of hexaphenylethane into two triphenylmethyls $(C_6H_5)_3C-C(C_6H_5)_3 \rightarrow 2C(C_6H_5)_3$ to be about 10 to 12 k. cal./mol. in different solvents. As opposed to this, the heat of activation for the decomposition, which proceeds as a monomolecular reaction, amounts to about 19 k. cal./mol. (at temperatures about 0° C.), and is therefore greater†.

The equilibrium degree of dissociation depends for different compounds on the aromatic or unsaturated substituents, and indeed the rule holds in general that the more bulky the substituent, the further to the side of the radicle lies the equilibrium point‡. Measurements of the heat of dissociation for radicles with trivalent C other than triphenylmethyl are not available up to the present.

Nothing need be said here as to the older attempts to interpret the stability of such radicles, which in any case led to contradiction§. (Theory of "valency requirements".) It need only be remarked that as early as 1928, Ingold|| gave an explanation which was based on mainly the same grounds as our theory, although it was not based on quantum theoretical calculations.

We illustrate the theory by the example of hexaphenylethane, on the basis of

* K. Ziegler and L. Ewald, *Ann. d. Chem.* **473**, 163 (1929). (It is possible that these values are too low by a small amount, about 1 k.cal.)

† K. Ziegler, P. Orth and K. Weber, *Ann. d. Chem.* **504**, 131 (1933).

‡ W. Schlenk, T. Weickel and A. Herzenstein, *Liebigs Ann.* **372**, 1 (1910).

§ On this matter, see e.g. W. Hückel, *Theoretische Grundlagen der organischen Chemie*.

|| C. K. Ingold, *Ann. Rep. Chem. Soc.* **25**, 154 (1928); H. Brixton and C. K. Ingold, *Proc. Phil. Soc. Leeds*, **1**, 421 (1929).

method II. In contrast to the earlier attempts at explanation, the theory assumes that the C—C linkage which unites the two radicles in hexaphenylethane does not differ materially in structure from the normal C—C linkage. Rather it assumes that the small heat of dissociation is due to the fact that, during the process of separation of the radicles, the energy content of the two triphenylmethyls diminishes, so that the expenditure of energy necessary for the rupture of the C—C linkage is mainly provided by this decrease of energy content. This "gain of energy" is interpreted* by quantum mechanics in the following manner. In hexaphenylethane, the four valencies proceeding from each of the middle C-atoms form a regular (or nearly regular) tetrahedral arrangement. The π -electrons of the phenyls attached to these two atoms cannot (or can only slightly) take part in the resonance coupling with the electrons of these C-atoms, owing to the symmetry of the eigenfunctions. When, however, the two radicles are separated, such a resonance is possible, and it is best from the energy point of view, when the radicle is plane. Then the electron which originally belonged to the C—C linkage has become a π -electron, and the plane arrangement is stabilized by the π -electron. Now the absolute value of the total resonant coupling in such an atomic arrangement is much greater than it is for three phenyl rings, whose π -electrons are isolated from each other in so far as resonance phenomena are concerned. Hence the gain of energy. The fact that the heat of activation is greater than the heat of dissociation† can easily be harmonized with this conception.

The increase of resonance energies can be taken from the data given in ²⁴table 1. The total resonance energy of a single $(C_6H_5)_3C$ before the dissociation is equal to that of three phenyls, i.e. -24β . After the dissociation, the resonance energy for a single triphenylmethyl is -25.794β . The gain per radicle is therefore 1.794β , and for the two radicles resulting from the dissociation it is 3.588β . With $\beta = 15$, this gives a gain of 55.77 , and with $\beta = 20$, a gain of 71.76 k. cal./mol. This increase is therefore in fact of the same order of magnitude as the work of separation of a C—C linkage. A quantitatively exact calculation of the energy of dissociation is not possible, since the structure of the σ -linkages proceeding from the central C-atom is changed in the dissociation, although the energy change concerned in these linkages will, it is true, be relatively small. On the other hand, the dependence on the substituents can be deduced with an accuracy corresponding to that with which β is known.

In general, the amount of energy which is gained by alteration of the resonance energy on the dissociation of a radicle we shall call the (static‡) "linkage demand" of the C—C linkage in the radicle, due to resonance of the π -electrons. If A_1 , A_2 are these linkage demands for the two radicles into which the molecule splits, then $A = A_1 + A_2$ is the total linkage demand of the C—C binding through resonance. Table 3(a) contains the values of A_i for a few radicles. They follow from the

* E. Hückel, lecture at the Baden and Württemberg meeting of the Deutsch. Physik. Ges. Jan. 1933; *Z. f. Phys.* **83**, 632 (1933). (Based on method II.) Nearly simultaneously and independently by L. Pauling and G. W. Wheland, *J. Chem. Phys.* **1**, 362 (1933). (By method I.)

† E. Hückel, *Z. f. Phys.* **83**, 674 et seq. (1933).

‡ In contrast to a "kinetic" linkage demand which can be defined for the heat of activation, see E. Hückel, *loc. cit.*

resonance energies given in table 1, in the same way as for triphenylmethyl. Table 3(b) contains the values of A_i for some symmetrical aromatically and aromatic-aliphatically substituted ethanes. It is seen at once that in the completely aromatically

Table 3(a). Static linkage demands A_i due to resonance in certain radicles

Radicle	$A_i = x\beta$	A_i in k. cal./mol., calculated for	
		$\beta = 15$	$\beta = 20$
3 aromatic substituents:			
C (Diph) ₃	1.859β	27.89	37.18
C (Diph) ₂ Ph	1.841β	27.62	36.82
C (Diph) (Ph) ₂	1.819β	27.29	36.38
C (Ph) ₃	1.794β	26.91	35.88
2 aromatic substituents: ¹			
C (Diph) ₂ Aliph	1.351β	20.27	27.02
C (Ph) ₂ Aliph	1.200β	18.00	24.00
1 aromatic substituent: ¹			
C (Diph) (Aliph) ₂	0.897β	13.46	17.94
C (Ph) (Aliph) ₂	0.720β	10.80	14.40
No aromatic substituents:			
C (Aliph) ₃	0β	0	0

¹ For brevity, the resonance energies for these radicles are not included in table 1.

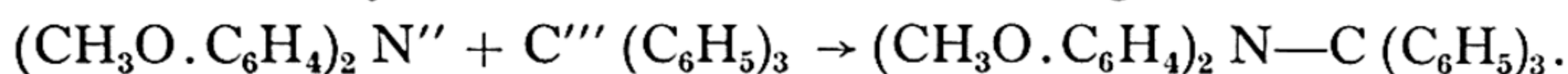
Table 3(b). Total linkage demand due to resonance, $A = 2A_i$,
for some symmetrically substituted ethanes

Compound	A	A in k. cal./mol. calculated for	
		$\beta = 15$	$\beta = 20$
(Diph) ₃ C—C (Diph) ₃	3.718β	55.77	74.36
(Diph) ₂ C—C (Diph) ₂ Ph Ph	3.682β	55.23	73.64
Diph C—C Diph (Ph) ₂ (Ph) ₂	3.638β	54.57	72.76
(Ph) ₃ C—C (Ph) ₃	3.588β	53.82	71.76
(Diph) ₂ C—C (Diph) ₂ Aliph Aliph	2.702β	40.53	54.04
(Ph) ₂ C—C (Ph) ₂ Aliph Aliph	2.600β	39.00	52.00
Diph C—C Diph (Aliph) ₂ (Aliph) ₂	1.794β	26.91	35.88
Ph C—C Ph (Aliph) ₂ (Aliph) ₂	1.400β	21.60	28.00
(Aliph) ₃ C—C (Aliph) ₃	0β	0	0
4.21 C (Ph) ₄ → C (Ph) ₃ + Ph	1.794β	26.91	35.88

substituted ethanes, the linkage demand increases with the bulk of the substituent, i.e. the energy of dissociation diminishes. The difference, for example, between tridiphenylmethyl and triphenylmethyl amounts to 0.130β , which gives the value 1.95 with $\beta = 15$ and 2.60 k. cal./mol. with $\beta = 20$. This is in harmony as regards

order of magnitude with the (not exactly known) difference between the dissociation constants of these compounds. Further, it can be deduced from table 3 that the substitution of only one aromatic substituent by an aliphatic one, reduces the linkage demand quite considerably, since this substituent can contribute nothing to the increase of resonance energy. This explains why stable free radicles are known only in completely aromatic or aromatic-unsaturated substituted C-atoms*. We see also, that radicles like allyl, $\text{CH}_2\text{—CH—CH}_2$, for example, cannot be stable. For the gain of resonance energy in the dissociation of the dimers is here much too small ($A = 2 \times 2.82\beta - 2 \times 2\beta = 1.64\beta$). Finally, in table 3(b), the linkage demand for dissociation of tetraphenylmethane is surveyed from the point of view why the dissociation does not take place, which the older theories of valency requirements could not explain. Here it appears that in the dissociation of a $\text{C—(C}_6\text{H}_5)$ linkage, only one of the resulting radicles gains resonance energy; in other words, that the linkage is only “unilaterally demanded.”

The theory can also remove other contradictions which were inherent in the older conceptions†. It is known that certain free radicles with trivalent C, and others with divalent N, each of which is stable by itself, i.e. the dimers of which tend to dissociate, will yet combine with each other, e.g.



The theory of valency requirements was not able to explain this. On the other hand, this behaviour fits naturally into our theory. If we represent the work of separation of the corresponding substitution bonds by (C—C) , (N—N) , (C—N) , then the conditions for the observed behaviour are expressed by

$$(\text{C—N}) > (\text{C—C}); \quad (\text{C—N}) > (\text{N—N}); \quad (\text{N—N}) \leq (\text{C—C}).$$

(The latter because the dimer of the nitrogen radicle is at least as strongly dissociated as hexaphenylethane.) Here experimentally $(\text{C—C}) \cong 11 \text{ k. cal./mol.}$

If further we denote the work of separation of the linkages, without taking account of the gain of resonance energy, by $(\text{C—C})_0$, $(\text{N—N})_0$, $(\text{C—N})_0$ and the linkage demands for the two radicles by A_C and A_N , then

$$\begin{aligned} (\text{C—C}) &= (\text{C—C})_0 - 2A_C \\ (\text{N—N}) &= (\text{N—N})_0 - 2A_N \\ (\text{C—N}) &= (\text{C—N})_0 - (A_C + A_N), \end{aligned}$$

and the above conditions become

$$\begin{aligned} (\text{C—C})_0 - (\text{C—N})_0 &< A_C - A_N \\ (\text{C—N})_0 - (\text{N—N})_0 &> A_C - A_N \\ (\text{C—C})_0 - (\text{N—N})_0 &\geq 2(A_C - A_N). \end{aligned}$$

If we take the linkage demands $A_C = 1.794\beta$ and $A_N = 1.200\beta$ (the latter is the value for a radicle C(Ph)_2 Aliph.; the actual linkage demand is possibly smaller),

* Whether the radicles with an aliphatic substituent like $(\text{C}_6\text{H}_5)_2 \text{C—CH}_3$, $(\text{C}_6\text{H}_5 \cdot \text{C}_6\text{H}_4)_2 \text{C—CH}_3$ observed by Conant and his collaborators are really stable, seems to us not definitely proved. (Cf. W. Hückel, *Theoret. Grundl. der org. Chemie*, 2nd edition, 1, 116, Leipzig (1934). Also J. B. Conant and N. M. Bigelow, *J. Amer. Chem. Soc.* 50, 2641 (1928), and J. B. Conant and R. W. Schultz, *ibid.* 55, 2098 (1933).)

† This was pointed out by Pauling.

and if we take, for the work of separation, the binding constants $(\text{C—C})_0 = 72.6$, $(\text{C—N})_0 = 68$ and $(\text{N—N})_0 = 32$, then with $\beta = 17.5$, all the requirements are fulfilled. There even remains a rather large margin for a change in the assumed values.

As mentioned above,¹⁵ Pauling and Wheland explain the stability of the radicles under discussion in practically the same way. They calculate only the energy increase which occurs in the dissociation by method I and interpret it then as a gain in "exchange energy." (They speak of a gain of "resonance energy," but this expression is to be differently interpreted than in method II; the exchange energy alters during the dissociation and we may describe this as an alteration of the "resonance" between the canonical structures.) In the calculation of this increase according to method I, they have indeed to simplify the procedure in a somewhat arbitrary fashion, owing to the extremely great number of canonical structures*. They find the right order of magnitude for the linkage demand, but a much greater dependence on the bulk of the substituent than can be reconciled with observation†. For example, they obtain a difference of 11.8 k. cal. between the heats of dissociation of hexaphenylethane and hexadiphenylethane, which is certainly much too great in view of the observed difference in the degree of dissociation.

The same cause, which we used to explain the small work of dissociation of two aromatic-substituted C-atoms, can also be made to explain why the heat of the transformation, Diamond-graphite, is so small. In the diamond-graphite transformation, half a diamond linkage is broken per C-atom. Consequently there results one π -electron for each atom in graphite, and the π -electrons in the individual slip planes of the graphite undergo resonance. The calculation of this coupling by method II for a single slip plane gives a continuum as the term spectrum for these electrons. One half of the states is binding, the other relaxing, by resonance. In the ground state, all the binding states are doubly occupied. The linkages cannot be localized. Within the lattice plane, the electrons have the character of conduction electrons. As mean resonance energy for a π -electron, we find -1.58β . If the work of separation per C—C linkage is taken as about 73 k. cal., then it must be taken as about 36.5 k. cal. per C-atom. On the other hand resonance energy is gained. With $\beta = 15$, this gain is calculated as 23.7, or with $\beta = 20$ as 31.6 k. cal./mol. It agrees therefore in order of magnitude with the work expended. Naturally, this is only quite a rough estimate, since:

(1) If the structure of the σ -linkage changes in the transformation, this will contribute to the energy change, and will be of relatively more importance than in the substituted ethanes.

(2) After the transformation, forces—although rather weak ones—still act between the slip planes, which depend on van der Waals' forces and on residual valencies. (Resonance action between the π -electrons of adjacent lattice planes.)

* This simplification consists in the main in the neglect of the "excited" structures, i.e. those for which non-adjacent atoms are connected by valency links.

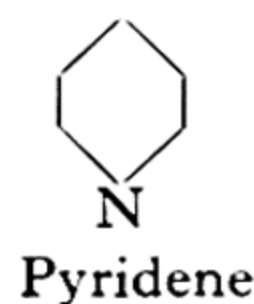
† In the original work, incorrect values were obtained at first. The value 11.8 k. cal. given here is taken from a correction given by Pauling and Wheland. [Note added in proof: For this correction see L. Pauling and G. W. Wheland, *J. Chem. Phys.* 2, 482 (1934).]

(3) The value of β in graphite may deviate from the value deduced from the energy contents of the aromatic compounds.

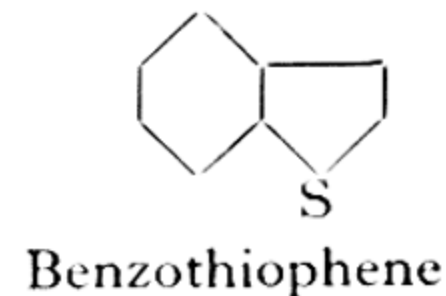
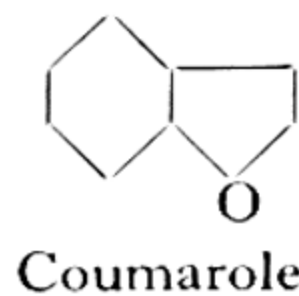
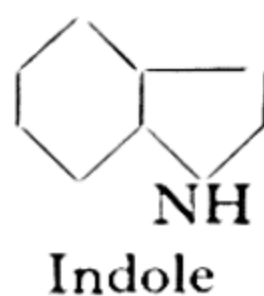
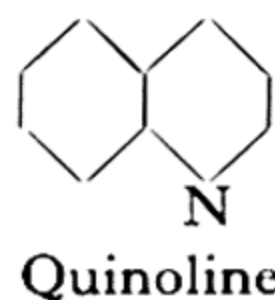
It would not be easy to take these points quantitatively into account, but it does not seem open to doubt that the conceptions developed here roughly deal with the essentials.

(c) *Discussion of chemical properties in relation to constitution*

The results of method II yield certain qualitative conclusions on a number of chemical properties. We consider first *Ring compounds, diphenyl and condensed systems*. From figure 3 it will be seen that the ring with 6 members, diphenyl and condensed systems, all differ from rings with 4, 8; 5, 7 members in that in the former compounds all π -electrons are in binding states which are fully occupied. We have here, therefore, closed electron groups. On the other hand, the 4 and 8 ring compounds have two electrons which neither bind nor separate, and also the highest occupied state, which is doubly degenerate, is not fully occupied. However, it is very improbable that in either of these rings the calculated electronic structure can have a real significance, since in them probably the atoms are no longer arranged in a plane, on account of the great deviation of the valency angles from 120° , which would be necessary for a plane structure. Consequently we shall not consider these rings further. (In any case, the 4 ring is unknown.) The 5 and 7 rings have no closed electron groups, and indeed in the 5 ring a binding state to close the group is lacking, whilst in the 7 ring a single electron is in a non-binding state. This accounts for the fact that the 5 ring, at least in the presence of a positive ion, has a tendency to take up one electron, which results in the existence of metal compounds like $[C_5H_5]^-K^+$ which are considered as of ionic character, whilst in the 7 ring no such compounds are known. Among the rings, the 6 ring is specially distinctive. This individuality exists also among heterocyclic rings. This arises, however, not on account of the number 6 of atoms in the ring, but on account of the number 6 of π -electrons. Such heterocyclic rings are, e.g.*



Corresponding to these we have, for example, the heterocyclic condensed ring-systems



which are analogous to naphthalene.

In these compounds, N brings *one* π -electron, NH, O and S bring two π -electrons into the ring, and the total number of 6 or 10 electrons forms a closed electron group. (In the corresponding compounds analogous to anthracene the

* For further details, see W. Hückel, *Theoret. Grundl.* 2nd edition, 1, 386, Leipzig (1934).

critical number is 14.) Naturally, the symmetry of the eigenfunctions and the eigenvalues of the π -electrons are distorted in these cases, though this does not affect the enumeration of the binding states. A quantitative treatment of such compounds has not yet been attempted.

The difference in behaviour between aromatic and unsaturated compounds is not easy to interpret, since the latter also have closed electron groups (see figure 3).

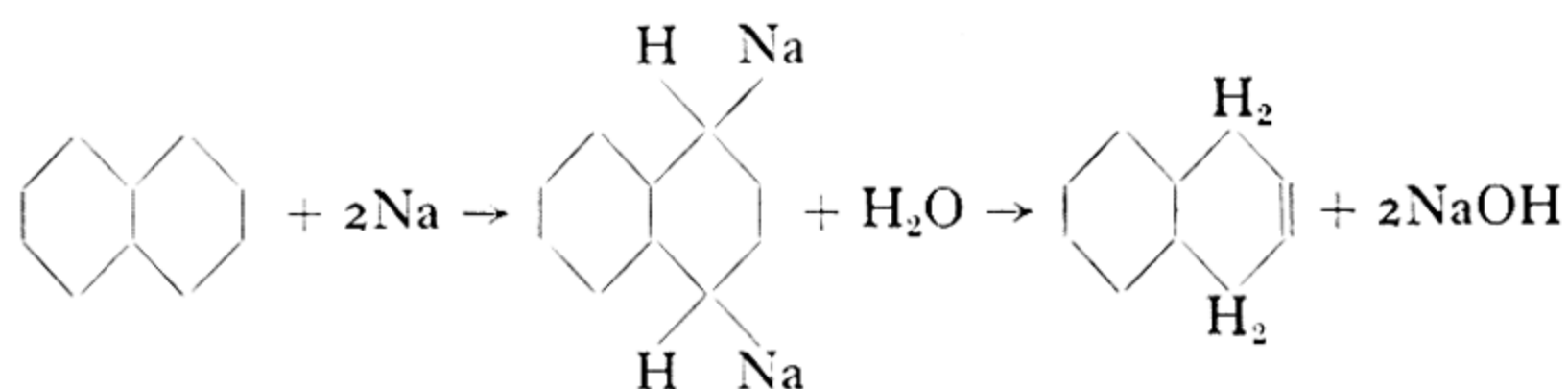
In free radicles, the highest state is not fully occupied, and indeed this state can be:

- (1) Neither binding nor relaxing (allyl, etc.; triphenylmethyl, etc.).
- (2) Binding [C_5H_5 , $C_5(C_6H_5)_5$].
- (3) Relaxing (C_7H_7).

The stable radicles like triphenylmethyl have on the one hand a tendency to gain an electron (forming a metal compound like $(C_6H_5)_3 C^- Na^+$, which is liable to dissociate into the ions $(C_6H_5)_3 C^-$ and Na^+). On the other hand, they have also a tendency to lose an electron (forming compounds like $(C_6H_5)_3 C^+ Cl^-$, which is liable to dissociate into $(C_6H_5)_3 C^+$ and Cl^-). These radicles therefore exhibit a behaviour which can be described as amphoteric.

The radicle C_5H_5 , which is not stable in itself, has no tendency to behave as a positive ion (its chlorine compound has no ion-forming character), corresponding to the fact that the highest occupied state is binding. On the contrary, as already mentioned, it forms compounds in which it can be regarded as a negative ion. It has therefore an electro-negative character. The stable pentaphenylcyclopentadienyl should also possess such a character, since in it also, the highest occupied state is binding, and it is one electron short of a closed group. Although as far as we are aware, there are no data on the electrochemical character of this radicle, we can refer to the fact that Ziegler* from other considerations concludes that this radicle should have a pronounced electro-negative character.

Some of the molecules with closed electron groups have, when alkalis are present, a tendency to take up electrons. They are to a greater or less degree in a condition to take up alkali metals, and then to become hydrogenated. Thus:



The ease with which the addition of one and the same alkali metal takes place, decreases in the following sequence. (The data are only qualitative.)

Anthracene easily adds Na and Li in the 9, 10 position.

Naphthalene adds Na slowly and Li faster, in the 1, 4 position. Conjugated double bonds (isoprene) add them in the 1, 4 position; Na about as fast as naphthalene, Li not investigated.

* K. Ziegler and B. Schnell, *Ann. d. Chem.* **445**, 266 (1925).

Phenanthrene adds Na very slowly, Li somewhat slower than naphthalene.

Diphenyl in the 1, 4 position*, adds Li but not Na.

Benzol and isolated double bonds add neither Na nor Li. Finally diphenylpolyenes add Na to the C-atom which is next to the phenyls, and do so rather easily. (One deduces the position of the addition, from the constitution of the products formed by hydrogenation, assuming that the hydrogenation occurs at the same place as that at which the metal is added.)

It now seems that there is a connexion between the sequence for ease of addition, and the sequence of resonance energies in the lowest unoccupied states (which can be doubly occupied!). This may be seen from figure 3, where the compounds are numbered according to the latter sequence. (Phenanthrene was not calculated. Diphenylpolyenes should also combine easily.) Moreover, there is a relation between the positions at which the addition occurs, and the charge distribution of the lowest unoccupied states, which in the presence of alkalis are occupied. The addition occurs namely in that position where this charge distribution has its maximum. This is so for all the cases mentioned where the calculation of the charge distribution has been carried out (anthracene, naphthalene, conjugated double bonds, diphenylpolyenes) with the exception of diphenyl. Here the greatest charge density is at the 4, 4 position, and we should therefore anticipate that the addition would occur at these points. In naphthalene, the charge density is the same at the positions 1, 4 and 5, 8. That the hydrogenation occurs only at the 1, 4 (or 5, 8) and not in (1, 8) or (4, 5) may be connected with the fact that for the latter case the resulting compounds have less favourable energy, and thus rearrange themselves to form 1, 4 dihydronaphthalene.

§ 6. CONCLUSION

As already mentioned, I have shown that a quantum-theoretical explanation can be given using method II, for the individual reactive behaviour of substituted benzenes ("induced polarities"). Consequently nothing further will be said here on this point. The relevant original work may be consulted†.

In general the theory has been so far developed that the employment of only one constant, the resonance integral β , is required. It is clear that with these ²³ limitations, only relatively rough conclusions as to the constitution and behaviour can be drawn. I believe, however, that I have shown that quite important progress has already been made towards the understanding of the compounds under consideration. On points for which a closer examination, which naturally must be much more complicated, would be necessary, I have given references at different points of the above outline.

The treatment of further properties, such as magnetism and light absorption, is a task for further research.

* According to W. Schlenk and E. Bergmann (*Ann. d. Chem.* 463, 1 (1929)) the addition should at least occur in the same phenyl, probably in the 1, 4 position. The argument for this seems to us not very cogent.

† E. Hückel, *Z. f. Phys.* 72, 310 (1931); see also *Nature*, June 25, 1932.

DESCRIPTION OF THE BINDING FORCES IN MOLECULES AND CRYSTAL LATTICES ON QUANTUM THEORY

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ABSTRACT. The distinction between heteropolar and homopolar bonds is briefly outlined. As regards the theoretical explanation of the phenomena we may obtain different degrees of a theory of cohering matter, according to the extent to which quantum theory is introduced into the basis of the theory.

A number of problems are then taken up in order.

(1) Why is hydrogen diatomic? To explain this it is necessary to show that when a number of electrons and a number of protons are brought together, the state of lowest energy is that in which the protons are associated in pairs, at a fixed distance apart, and that two electrons are associated with them. Various methods of approximating to the solution of the mathematical problem involved are discussed, and it is emphasized that all of them rest on "models."

(2) Why is H₂O bent, and indeed why is such an angle characteristic of a large group of oxygen compounds? The discussion of this problem leads to a consideration of the distinction between a valency link binding and a (homopolar) binding not describable by valency links.

(3) Why is Na a metal, but Cl a gas, although both are univalent? Under this heading are discussed, among other points, the conditions which favour lattice formation as a state of lowest energy.

(4) Why do solid insulators occur, like the diamond? In other words, the problem is that of explaining the existence of non-ionic lattices with strong binding.

(5) How are the transition cases like arsenic to be classified?

Finally, it is pointed out that we cannot yet calculate in general when Nature will use one sort of binding, and when the other. Consequently a survey of the types of aggregation actually met with in the elements is of interest, and a diagram showing this is provided.

§ 1. EMPIRICAL

To obtain a concise survey of the *cohesive properties of matter in bulk*, we will arrange the simple substances with respect to the strength with which they cohere and to other obvious properties.

The quite coarse classification into those substances which at ordinary temperatures are solid and those which are gases (among simple substances, only water and mercury are liquid) shows two great groups of forces which hold together the lattice of the solid state. If we include electrical conductivity as noteworthy, we obtain the following schematic survey:

	Examples	Melting point	Solid state	
Rare gases	He, Ne ...	Very low	Insulators	Atomic lattice
Polyatomic gases	H ₂ , N ₂ , O ₂ F ₂ , Cl ₂ , ... CH ₄ CO, CO ₂ HCl, H ₂ O, NH ₃			Molecular lattice
Salts	LiF, ... CsI, MgO, ... CaF ₂	High	Insulators to electrolytic conductors	Ionic lattice
Metals	Na, Mg, Al... Fe ScN, TiC	Metallic conductors	Atomic lattice
Compounds of the nature of the diamond	Diamond, Si, B? SiC, BN	Very high	Insulators	

To those properties of the simplest substances collected in the table, we have to add the general system of ideas which chemistry has abstracted from its enormous empirical material. As limiting cases between which there are transitional cases, we have heteropolar and homopolar bonds. Heteropolar compounds in the ideal case form solid bodies at ordinary temperatures (we do not consider here the case of solutions). A characteristic integer can be attached to the individual atoms and it may be either positive or negative. In compounds, the sum of these numbers is zero even in a comparatively small region. In addition it would seem that the atomic arrangement in the crystal lattice is mainly determined by the relative "sizes" of the atoms. If we extend our considerations to cases like NaCl vapour, or (more remote from the ideal case) HCl and NH₃ gas, then we find molecules; in them the atoms are so constituted that the sum of the characteristic numbers (to call them valency numbers departs probably from the language of the chemist) is zero.

In homopolar compounds, which form molecules in the simple cases, the atom has a valency number, an integer which has no sign; multiple valencies of an atom have fixed directions to each other (tetrahedral for the C-, plane angle for the O-atom). "The valencies saturate each other mutually," a valency from one atom combining with a valency from a neighbouring atom to form a valency link.

§ 2. THEORETICAL BASIS

The atom as a stable dynamical system of charged particles is inexplicable to classical physics. According to the extent to which we apply quantum theory, whether we only introduce general facts of the quantum theory, and think, in the main, on classical lines, or whether we employ complete quantum mechanics for the phenomena, we obtain *different degrees of a theory of cohering matter*.

As a first and rather crude step we consider atoms as given and assume forces between them, repulsive on account of the impenetrability, attractive on account of the electrical structure of the atom. To this stage belongs the classical kinetic theory

of matter, van der Waals' explanation of the relation between the liquid and gaseous states, and Debye's explanation of the constants in van der Waals' equation. This step in the theory did not explain the special properties of different substances, nor, above all, the rules of chemistry.

At a more advanced stage the individual properties of atoms, such as the existence and energy of positive or negative atomic ions, are deduced from the quantum theory of the atom. The aggregation of matter is then explained as being due to the electrostatic forces between the ions, so that the explanation is classical and pictorial. To this stage belong Kossel's explanation of heteropolar chemistry and Born's theory of the atomic lattice. The chief points left unexplained are homopolar molecules, metals, and certain solid insulators like diamond.

In the third stage, the quantum theory of the molecule and the crystal lattice, electrons are regarded as moving in a system of a few nuclei (as in molecules) or of many nuclei (as in crystal lattices) in a non-classical and non-pictorial manner by the methods of the (non-relativistic) quantum mechanics initiated by Heisenberg and Schrödinger (1925-26). This stage of development leaves most of the results of the earlier stages untouched; however, it adds some new results, and explains the properties of aggregated substances which are not explicable on classical, pictorial lines, viz. homopolar chemistry and solid atomic lattices (metals, and substances of the diamond type).

§ 3. THEORY OF HOMOPOLAR BINDING IN MOLECULES AND CRYSTALS

We illustrate certain important features of the theory by examples.

Why is hydrogen diatomic? In order to explain the diatomic nature, we must calculate that the energy of the lowest state of a system of two electrons in the field of force of two rigidly fixed H-nuclei has a minimum at a certain finite separation of these nuclei. Further we must calculate that the energy of the lowest level of a system of three electrons in the field of force of three rigidly fixed H-nuclei has a minimum when two of the nuclei have a certain fixed distance, and the third is remote from them. Heitler and London calculated out the system with two nuclei by an approximation method which started from the ground state of two separate atoms each with one electron. The principal feature is the classically unexplained splitting of the energy into two energy levels (i.e. terms), as we proceed from widely separated to closely approaching nuclei. In this process, one of the terms goes to lower values, and finally reaches a minimum, whilst the other tends upwards. London studied the addition of a third atom to this assembly: the lower energy level does not split further; there is no means for the energy to decrease further on closer approach of the third nucleus. The valencies of both original atoms were "saturated," giving rise to a condition which led to no further splitting.

Another method of studying the same problem is the following: we can obtain approximately the condition of a single electron in the field of force of two or more nuclei by a kind of interpolation between the states for widely separated nuclei (when the electron behaves as the atomic electron near one nucleus) and

for slightly separated nuclei (when the state of the electron may be approximately obtained from the state in an atom, whose nuclear charge originates from coalescence of the nuclei). The lowest state of the single electron is diminished on bringing together the widely separated nuclei. The state of a system with many electrons is in this method approximated through the states of the individual electrons (this is also the route by which the atomic spectra were first understood). Then according to Pauli's principle, every (non-degenerate) state contains at the most two electrons. Thus in H_2 , two electrons can be brought into the lower level; in H_3 , one electron would have to be in a higher energy state (compare the relations in the He- and Li-atoms).

Both these concepts of binding in H_2 and of saturation have been generalized: the former to the spin-valency theory of London, Heitler and others, and by a further refinement of Slater's, whilst the latter has been extended to questions of chemical binding by Herzberg and Lennard-Jones. The method (a) of spin valencies, which builds the proper functions of the ground level of the molecule out of the proper functions of the ground levels of the individual atoms (not the individual electrons of this atom), shows which characteristics of the quantum mechanical description correspond to the concepts of "valency number" and "saturation." Slater's method (b), which builds the proper functions of the ground state of the molecule out of the proper functions of the individual electrons in the atom, can deal with cases which are too complicated for treatment by method (a). It brings out criteria of the quantum mechanical description which correspond to the chemical concepts of "valency angle" and "valency bond." Methods (a) and (b) (which do not differ in this matter) are applied by Heisenberg to the explanation of ferromagnetism on quantum theory.

Method (c), which builds the proper functions of the lowest state of the molecule out of the proper functions of the individual electrons in the field of force of this molecule, may not be so accurate, but is essentially simpler than Slater's method. It also embodies a quantum-mechanical description of the valency angle and valency bonds. It can be applied to the treatment of many properties of crystal lattices, especially metals. Its simplest form is then Sommerfeld's conception of free electrons. A more general form is Bloch's treatment of single electrons in periodic fields of force. In that case, the proper functions of the individual electrons are waves with a propagation vector k . If the energy of the state of the single electron can be approximated in the form $E = \frac{1}{2m'} k^2$ (and this is often the case), then $E = \frac{m'}{2} v^2$, where v is the "group velocity"; in this case the system of electrons can be treated as a system of free particles with an "apparent" mass m' .

All three conceptions rest on "Models," i.e. on simplified statements of the properties of actual molecules. Properties which in themselves are not negligibly small, but which are not important for the phenomena treated, are left aside.

Why is H_2O bent? The theory of heteropolar bindings could explain such an angle as due to the polarizability of the O-ion, but not the appearance of such an

angle as a general characteristic of a large group of O-compounds. Slater and Pauling showed by means of the above described method (b) that the quantum theory of homopolar molecules also leads to a (probably corresponding) understanding of this angle (as a property of the valencies of the O-atom). The angle can also be explained by method (c): let us take two nuclei, which individually can take up an s -electron in the lowest state, and an atom residue which possesses two p -electrons in the lowest state (p^2 , so that instead of the two p -“gaps” of the O-atom we take two p -electrons), then it can be shown that in the “straight” arrangement $s \dots p^2 \dots s$, only one energy level (which can hold two electrons) of lowest energy occurs. The two further electrons must enter a higher state. With the “bent” arrangement $s \nearrow p^2 \searrow s$ on the other hand, there are two neighbouring conditions of low energy for the four electrons, with approximately the same energy. With only a very slight alteration of the description, we obtain two coincident energy states for the single electrons; the proper function of the one differs appreciably from zero at the middle atom (p^2), at one of the end atoms (s) and between the two ($s - p^2$); that of the other differs appreciably from zero at the middle atom, at the other end atom and between the two. This state of affairs is the quantum mechanical description of the two valency links. In our example, the binding with valency links is describable in the sense of the quantum theory for the bent arrangement but not for the straight. If the p^2 atom enters with both its valencies into a combination which is describable with valency links, and in which s -atoms are attached at the ends of the links, then the latter must form an angle.

Slater's treatment, and that sketched above by method (c), provide a *quantum mechanical description of valency links*. From the point of view of method (c), a connexion with valency links is made when the proper function of the ground state of the molecule is approximated by such proper functions of the individual electrons as are only appreciably different from zero between and at two neighbouring atoms. Every orbital of an electron described by such a proper function is doubly occupied. On account of the model character of our representation, we cannot generally prove that a state of a molecule (or of a crystal lattice) described by valency links is always the lowest energy state. For an estimate which shall show that the bent state of H_2O with valency links has lower energy than the deepest state of a straight H_2O whose proper function is described otherwise, doubtful simplifications must be made. We must not be surprised if Nature in some cases which are analogous to our example shows us bindings which are not describable by valency links. In fact, these occur, as the binding in metal lattices shows; also the benzene ring, aromatic rings in general, and the graphite lattice are examples of structures not describable by valency links. The “*valency link binding*,” as we will call the above-described types, is therefore a concept exactly describable by quantum mechanics. How far Nature utilizes it, we cannot always calculate. The other kind of homopolar binding, where, in method (c), the proper functions of the individual electrons cannot be so constructed that they belong to two neighbours, obtains its *binding energy from the same unpictorial and non-classical features of the*

theory, and is therefore closely related to the valency link binding. The energies are also of the same order of magnitude. Differences in other respects (conductivity of metals, certain properties of the aromatic ring), justify, however, a conceptual *difference between a valency link binding and a (homopolar) binding not describable by valency links*.

Why is Na a metal and Cl a gas? The wholly different ways in which Na-atoms and Cl-atoms (at low and ordinary temperatures) become aggregated in the material in bulk, although they are both monovalent atoms, is an example of the fact that Nature utilizes the possibilities of valency link binding as well as the other homopolar possibility. The quantum mechanical treatment had to compare the model of a system of electrons in the field of force of the same number of regularly ordered (maybe space-centred cubic) atomic residues with charge $+e$, with the model where these electrons moved in the field of force of neighbouring pairs of residues, which otherwise were at great distances from each other. For the low terms, in contrast to the case of individual free atoms, the deviation of the quantum mechanics from the classical mechanics is important in both cases, as the Heitler-London calculation of the term separation for H_2 or the possibility of interpolation of the electron term in the molecule between two atomic states, showed earlier.

The large number of neighbours which an atom has is favourable to the lattice—in the normal metal, an atom has twelve or eight neighbours (fourteen if we include those only slightly farther away). For the molecule, it is favourable that a valency link should give a greater contribution to the binding than a pair of neighbours in the lattice. Since our approximation methods are of no further use for the distance relations which actually occur, the deductions must remain qualitative; we cannot therefore show deductively, why Na forms a solid lattice and Cl forms molecules. Yet there are certain circumstances which seem to favour the lattice arrangement in Na rather than in Cl. The s-proper functions of the Na-atom, on account of their spherical symmetry, can better utilize the advantage of the neighbours on every side than the *p*-“gaps” of the Cl-atom.

Why do solid insulators with atomic lattices occur, like the diamond? For the electrical conductivity of metals, it is important that a continuum of terms should belong to the lowest state of the multi-centred system corresponding to the lattice, and that at indefinitely small departures from the ground term there should be states which produce an electric current. Lattices composed of saturated molecules and of ions of rare-gas type are insulators, since the ground term is a single and isolated one. To understand the existence of non-ionic lattices with strong binding, we must show that in other cases the ground term of the crystal can be a single and isolated one. In method (c) this follows from the fact that the levels of the individual electrons, which form a continuum, have a finite gap exactly at the place up to which the states are occupied.

We can make this clear by a one-dimensional model. The electrons of the atoms, of which the chain lying in the x direction is to consist, are to be in *s*- and *p*-states. The *s*-proper functions are symmetrical with respect to the nuclei, in their dependence on x , whilst the *p*-proper functions are antisymmetric (figure 1).

We shall assume an s - and a p -state to be neighbours on an energy scale; we exclude degeneration of the p -state itself. With this simplification, the "periodic system" of the elements has periods of four, and consequently four electrons can be brought into the s - and p -states of a level. If we consider now the individual electrons in the complete chain system, as far as they are built out of the s - and p -states considered, we obtain the scheme shown in figure 2, for the energy of the individual electrons, as a function of a quantum number k , which is connected with the translatory properties of the chain (as shown by Bloch). When considering solely the s -states or the p -states of the separate atoms, the dotted curves were obtained (Bloch's curves) for the electrons of the chain, but taking both into account, the continuous curves are obtained. Each of the curves contains as many states as the chain has atoms; according to the Pauli principle, twice as many electrons can occur therein. The lower states of the individual electrons (roughly speaking, those in the lower curve) contribute to the binding, and those in the higher states tend to relax it.

If each atom of the chain brings an electron with it, half the states of the lower curve are occupied (figure 3a); we obtain *binding*. The limits up to which the states are occupied lie (for a chain with many members) in a continuum. If every atom of the chain brings two electrons with it, plainly the lower curve is fully occupied (figure 3b); we obtain *strong binding*. In this case it is not possible with a small expenditure of energy to produce another distribution of electrons. We have therefore an *insulator*, whose properties correspond to those of the diamond. If every atom brings three electrons, then half the upper curve is also occupied (figure 3c); the strong binding is relaxed again; in this case we have a *metal*. When every atom is accompanied by four electrons, the upper curve as well as the lower is fully occupied (figure 3d); we have an *insulator*. Moreover, the binding is yet further relaxed. We obtain, as would be expected, the loose lattice of a "*rare gas*."

When we attempt to extend the model to more dimensions, we see that for the occurrence of states in the insulator with strong binding, it is important that the binding in its lattice should be interpretable as valency link binding. According to their lattice structure and the valency numbers of their atoms, diamond, Si, SiC, Ge, one form of Sn, and BN belong to this class. As transition cases in this neighbourhood, lie some of the modifications of As, Sb, Bi, Se and Te. That some of these are metals is due to the fact that the relations of the model are disturbed by other terms, and is (especially for the higher atomic numbers) not to be wondered at.

How are the transition cases As, Sb, Si, Se, Te to be classified? We shall generalize our model of the uni-dimensional chain somewhat in that, by utilizing the y -direction, we place at the disposal of the electrons of the individually separated atoms, one s - and two coincident p -states. The s will be spherically symmetrical, one of the p -proper functions (p_x) will have a node perpendicular to the x -direction, the other (p_y) will result from it by rotating the x -direction to the y -direction. A period of the "periodic system" of the elements will then comprise six atoms; the rare gases are first reached when the atom has six electrons. The term scheme of the electrons in the chain is then that of figure 4. The newly added curve corresponds to the p_y -

states. It can happen that its lowest point lies above or below the highest point of the lower curve. In every case, if each atom is accompanied by one electron, we obtain a *metal*. If each atom brings with it three, four or five electrons, we also obtain a *metal*; the binding strengths diminish with four and five electrons. If every atom is responsible for six electrons, we obtain a loose *rare-gas lattice*. In the case where there is a gap between the middle and lower curves, we obtain, if each atom brings with it two electrons, an *insulator with strong binding forces of cohesion*

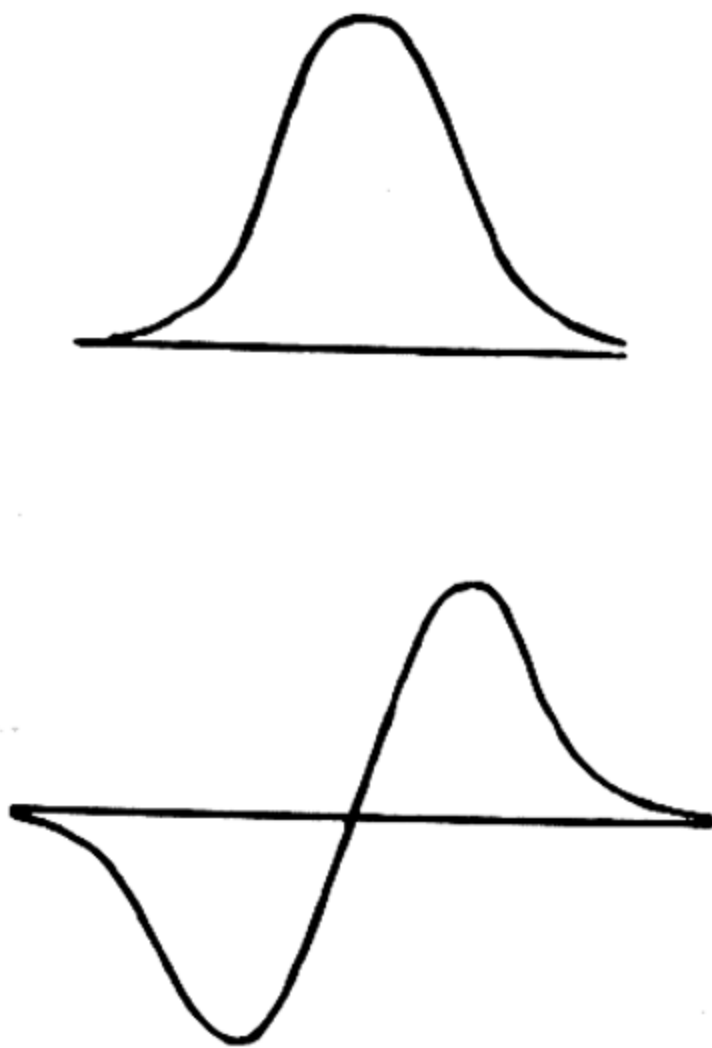


Figure 1. s - and p -proper functions of the model.

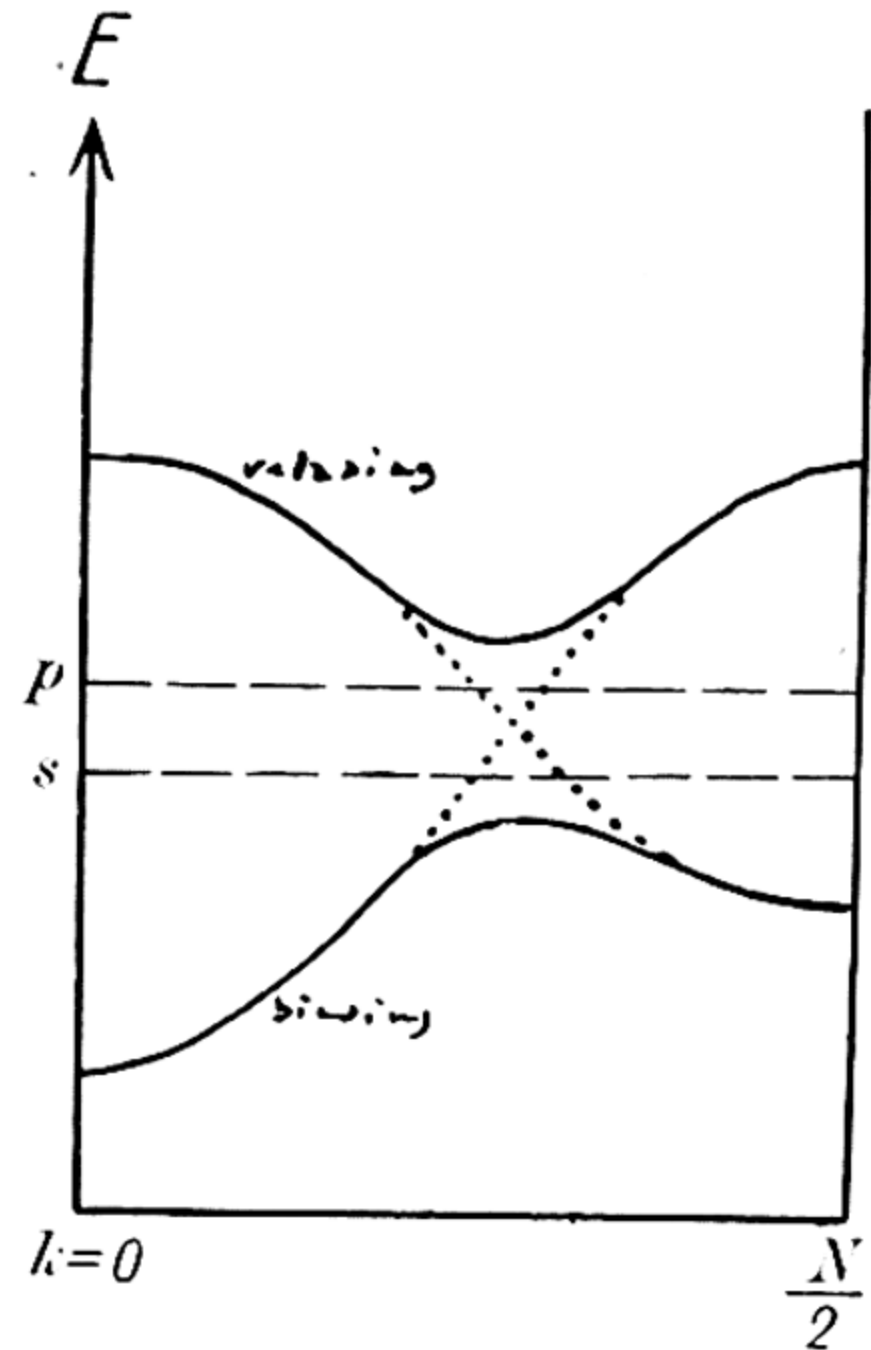


Figure 2. (From Hund, *Z. f. Phys.* 74, 7 (1932).) Energy values of the model.

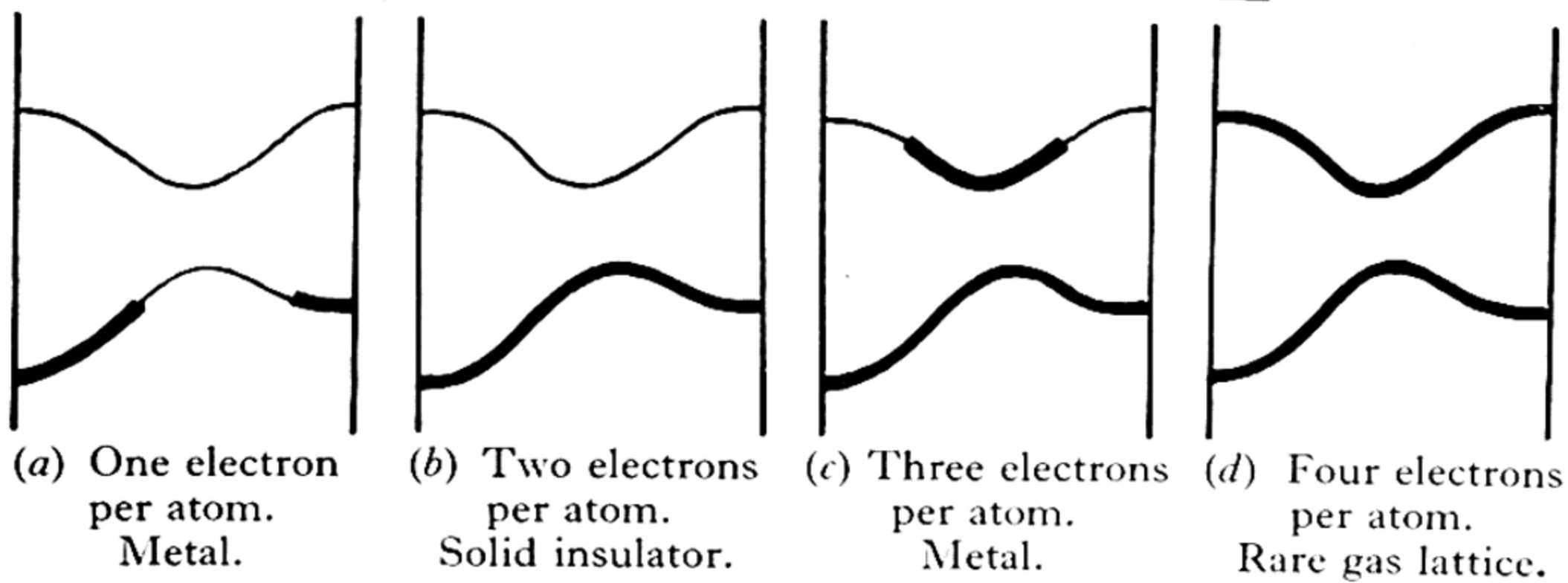


Figure 3. (From Hund, *Zs. f. Phys.* 74, 8 (1932).) Occupied states of the model.

(if the gap is small, the substance is a semi-conductor). In the case where the energy range of the middle curve overlaps that of the lower, there is, if every atom is accompanied by two electrons, a part from the lower area which remains free, and from the middle one a part which is occupied. We obtain a *metal with peculiar properties*. For cohesion, the overlap, if it is not too big, is without effect; it can therefore be described with reference to the states of the lower curve alone (valency link binding). The conduction properties can be so described, that the middle region has certain conduction electrons, and the lower region certain gaps, which in many respects behave like conduction electrons.

The application of the model to three dimensions shows that for the transition cases between an insulator with strong binding and a metal, it is important that the lattice should be representable as a valency link lattice (that therefore each atom should have as many outer electrons as there are valency links proceeding from it) but that for the electrons of the atom, states should be available, which do not enter into the valency link binding. The lattices of As, Sb, Bi seem from their structure to belong to this type. They may be so represented that every atom is connected by just one valency link to its three nearest neighbours. The three valencies proceed, not from

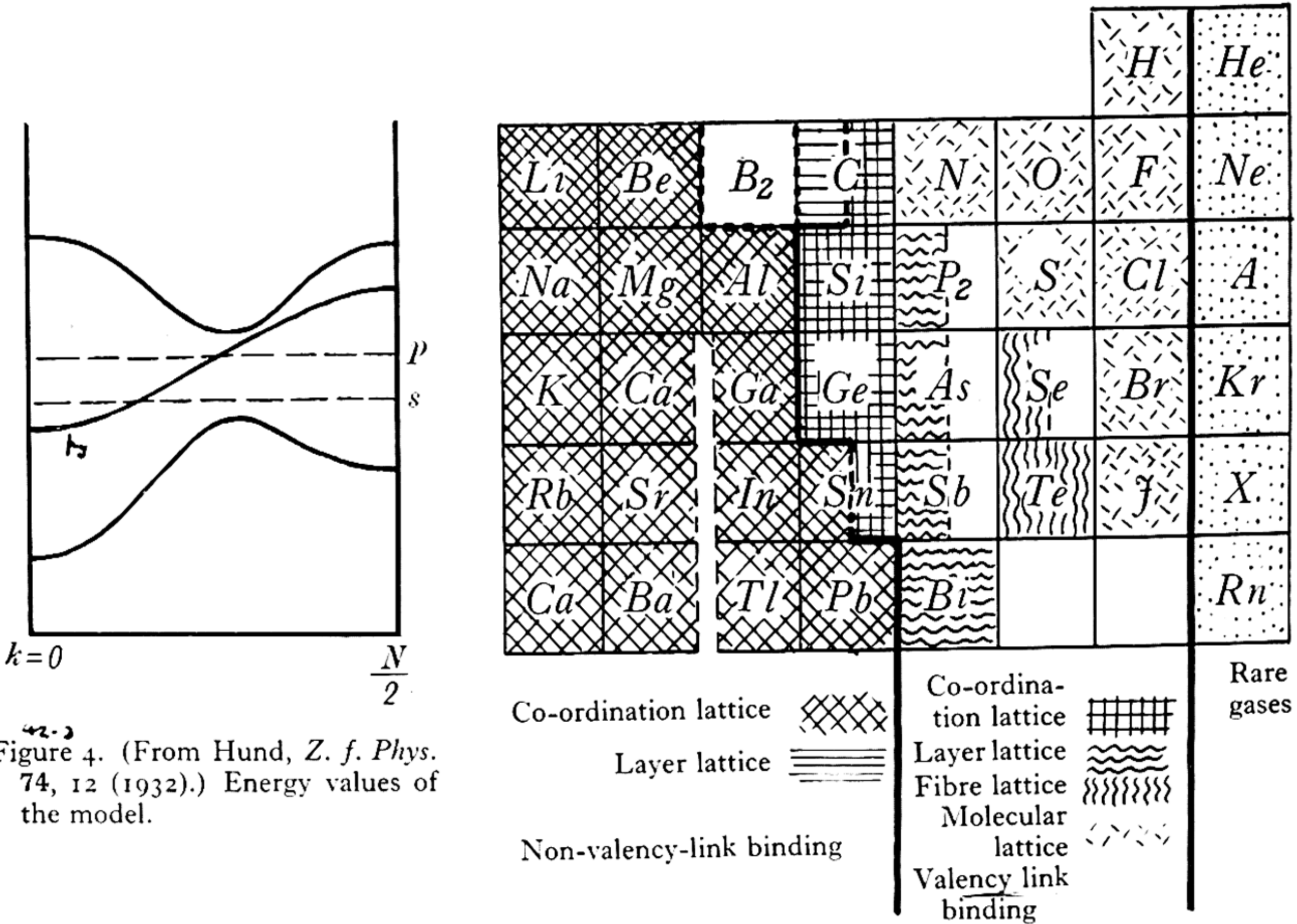


Figure 4. (From Hund, *Z. f. Phys.* 74, 12 (1932).) Energy values of the model.

Figure 5. (From Hund, *Handbuch d. Physik*, vol. 24, 1, p. 693.) Forms of binding in the elements.

three outer electrons, but from three gaps. We will however, for simplicity, speak of electrons. The valency angles are explained because the valency links can be described by means of the proper functions of the three p -states (in Slater's sense, or in that of method(c)). Now we can, in addition, form proper functions of the electrons in the lattice from the proper functions of the s -states. It appears that these energies overlap somewhat the energies of the valency link states, so that some of the former are occupied, and some of the latter unoccupied. It is probably because of this that many properties of bismuth are only explicable if we assume a very small number of free electrons.

§ 4. SURVEY OF THE TYPES OF BINDING IN THE ELEMENTS

We cannot calculate quantitatively when Nature will make use of one kind of strong homopolar binding (for which a description must use non-classical methods)—i.e. valency link binding—and when she will use the other. A collection of the relations actually found is interesting. Figure 5 gives a survey of the combinations in the elements, and therefore in aggregated material consisting of unmixed similar atoms. In the usual arrangement of the periodic system of the elements, the groups Sc to Zn, Y to Cd, La to Hg are neglected; they should not be differentiated from their surroundings in type of binding. On the “left” side we have the type of binding not to be described with valency links; on the “right” side, the valency link binding. Sub-cases occur since molecules can aggregate in one-dimensional or in two- or three-dimensional formations with valency links (molecular, fibre, layer or co-ordination lattices).

ATOMIC DISTANCES IN ORGANIC COMPOUNDS BY X-RAY ANALYSIS

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ABSTRACT. Tables are given for the distances between the atoms or groups in diamond, graphite and a number of organic compounds. In the case of more complex structures, the results are classified according as the values were determined from Fourier projections in three independent directions, or by some less complete analysis.

IN the following tables an attempt has been made to classify the X-ray data on atomic distances in organic compounds according to the intensiveness of the analyses from which they are derived. Generally it is only in the case of the elements themselves (Table I) that the structures are sufficiently simple for the interatomic distances to be derived directly from the lattice constants of the crystal; then, of course, the

Table I. Elementary structures

	Interatomic distances (Å.)		
Diamond*	C—C	1.541	C...C between layers 3.41
Graphite†	C—C	1.42	

* W. H. Bragg and W. L. Bragg, *Proc. R. S. A*, **89**, 277 (1913). W. Ehrenberg, *Z. f. Kristall.* **63**, 320 (1926).

† J. D. Bernal, *Proc. R. S. A*, **106**, 749 (1924).

determination of distance is equivalent to the determination of wave length with the crystal as a grating.

In all ordinary organic compounds the asymmetric crystal unit is a group of atoms comprising part of the molecule, the whole molecule, or, in a few cases, several molecules. The precise position of each atom, and hence its distance from its neighbour, can then only be determined by the simultaneous evaluation of a number of parameters. The task usually appears rather hopeless in the case of complex structures, and probably would be were it not for the very extensive knowledge of the relative position and arrangement of atoms contained in the structural formulae of organic chemistry. These provide a framework and it remains to make this framework metrical and to deduce its orientation in the crystal. But in a complex structure it is practically impossible to disentangle the effects upon the calculated values of the intensities due to varying certain interatomic distances or to altering slightly the orientation of the model with respect to the crystal axes. When the work reaches this stage, the method of Fourier analysis is invaluable, because it presents a picture of

the structure which is built up from the experimental measurements, only the phase constants of the terms being taken from a preliminary trial and error analysis. This means that approximations to the structure differing slightly in orientation or in

Table 2. Layer structures and linear structures. Atoms all in one crystal plane, or dominantly along one crystal axis

	Interatomic distances (Å.)	Intermolecular distances (Å.) (minimum)
Cyanuric triazide* (one Fourier projection)	C—N in ring 1·38	N...N 3·12
„	C—N outside ring 1·39	
„	N≡N terminal 1·11	
„	N=N 1·26	
Hexamethylbenzene† (Trial and Error Analysis)	C—C aromatic 1·42	CH ₂ ...CH ₂ 3·6–3·9
„	C—CH ₃ aromatic-aliphatic 1·48	
n-Hydrocarbon‡, C ₂₉ H ₆₀	CH ₂ —CH ₂ aliphatic 1·553§	
Hydrocarbon series‡	CH ₂ —CH ₂ aliphatic 1·534	

* I. E. Knaggs. (Report in preparation.)

† K. Lonsdale, *Proc. R. S. A*, **123**, 494 (1929).

‡ A. Muller, *Proc. R. S. A*, **120**, 437 (1928).

§ Assuming tetrahedral angle.

Table 3. Complex structures. Analyses based on three separate Fourier projections

	Interatomic distances (Å.)	Intermolecular distances (Å.) (minimum)
Anthracene*	C—C aromatic 1·41	CH...CH 3·7
Naphthalene†	C—C aromatic 1·41	CH...CH 3·6
Durene‡	C—C aromatic 1·41	CH ₃ ...CH ₃ 3·9
„	C—CH ₃ aromatic-aliphatic 1·47	
Dibenzyl§	C—C aromatic 1·41	CH...CH 3·7
„	CH ₂ —CH ₂ aliphatic 1·58	CH ₂ ...CH 4·1
„	C—CH ₂ aromatic-aliphatic 1·47	
Benzoquinone	C—C in ring ~1·5	—O...—O 3·62
„	C=C in ring ~1·32	—O...CH 3·36
„	C=O ~1·14	C...CH 3·44

* J. M. Robertson, *Proc. R. S. A*, **140**, 79 (1933).

† J. M. Robertson, *Proc. R. S. A*, **142**, 674 (1933).

‡ J. M. Robertson, *Proc. R. S. A*, **141**, 594 (1933); **142**, 659 (1933).

§ J. M. Robertson, *Proc. R. S. A*, **146**, 473 (1934); *Nature*, **134**, 381 (1934); (and report in preparation).

|| J. M. Robertson, *Nature*, **134**, 138 (1934); (and report in preparation).

atomic distances will all lead to the same final result, which has, therefore, the quality of a direct determination.

A double Fourier series is now generally employed, giving a projection of the structure in a certain direction. By piecing together the results of two or more pro-

jections of this kind, the whole structure can often be determined (Table 3). In the very rare cases in which all the atoms of the structure lie in one plane, a single projection perpendicular to this plane may sometimes give all the necessary information (Table 2). As the work is rather laborious, structures are sometimes satisfactorily determined by making a single Fourier projection and combining the

Table 4. Complex structures. Trial and error analysis combined with one Fourier projection

	Interatomic distances (Å.)	Intermolecular distances (Å.) (minimum)
Chrysene*	C—C aromatic 1·41	CH...CH 3·4
<i>p</i> -Diphenylbenzene†	C—C aromatic 1·42	CH...CH 3·9
Hexachlorobenzene‡	C—C between rings 1·48	
Urea§¶	C—Cl > 1·79	NH ₂ ...=O 3·2
Thiourea	C—NH ₂ 1·37	
„	C=O 1·25	NH ₂ ..NH ₂ 3·8
„	C—NH ₂ 1·35	NH ₂ ..=S 3·4
„	C=S 1·64	

* J. Iball, *Proc. R. S. A*, 146, 140 (1934).

† L. W. Pickett, *Proc. R. S. A*, 142, 333 (1933).

‡ K. Lonsdale, *Proc. R. S. A*, 133, 536 (1931).

§ Wyckoff, *Z. f. Kristall.* 81, 102 (1932); Hendricks, *J. Amer. Chem. Soc.* 50, 2455 (1928).

|| Wyckoff and Corey, *Z. f. Kristall.* 81, 386 (1932).

¶ Wyckoff and Corey, *Z. f. Kristall.* 89, 462 (1934).

Table 5. Complex structures. Trial and error analysis only

	Interatomic distances (Å.)
Hexamethylenetetramine (cubic)*	CH ₂ —N 1·42
β -Benzene hexabromide (cubic)†	CH—Br 1·94§
Diphenyl‡	C—C aromatic 1·42
„	C—C between rings 1·48

* Dickinson and Raymond, *J. Amer. Chem. Soc.* 45, 22 (1923).

† Dickinson and Bilicke, *J. Amer. Chem. Soc.* 50, 764 (1928).

‡ Dhar, *Indian J. Phys.* 7, 43 (1932).

§ Assuming tetrahedral cyclohexane ring.

|| Wyckoff and Corey, *Z. f. Kristall.* 89, 462 (1934).

measurements obtained with previous knowledge of the true interatomic distances, in order to calculate the precise orientation of the molecules in the crystal (Table 4).

Interatomic distance is, of course, only one aspect of the results of a complete structure determination. Precise information can be obtained about such stereochemical matters as valency angles, and the position taken up in the crystal by certain groups where free rotation is possible about a single bond. Some examples are shown in the following diagrams.

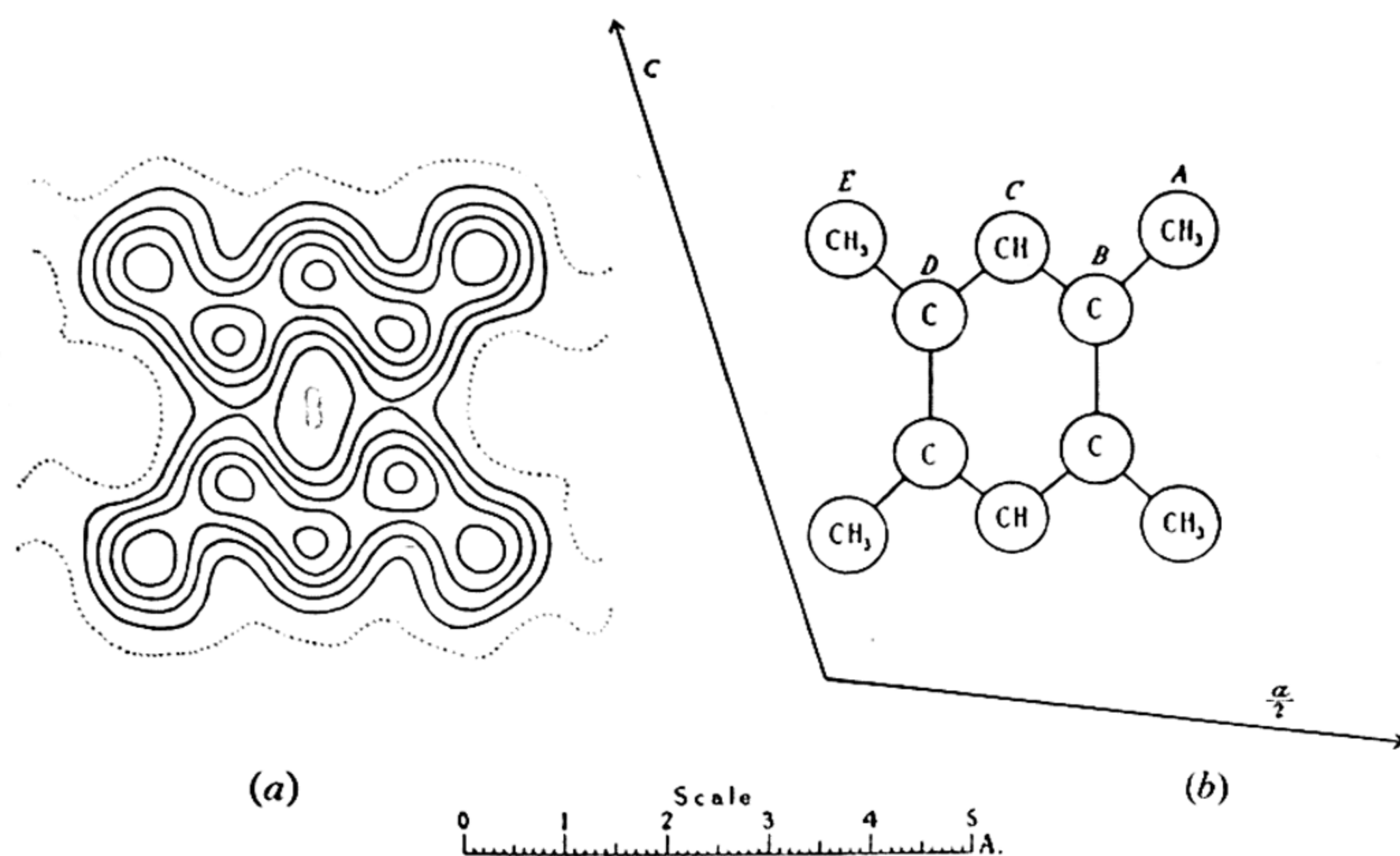


Figure 1. Durene (tetramethyl benzene) projected along the b axis. (a) shows the distribution of electron density by Fourier analysis and (b) is a diagram of the relative positions of the atoms in the structure. Each contour line represents a density increment of one electron per square Å. It is found that the methyl groups are displaced away from each other by about 3° beyond the symmetrical position. The plane of the ring is, of course, inclined to the line of projection, thus distorting it from a regular hexagon.

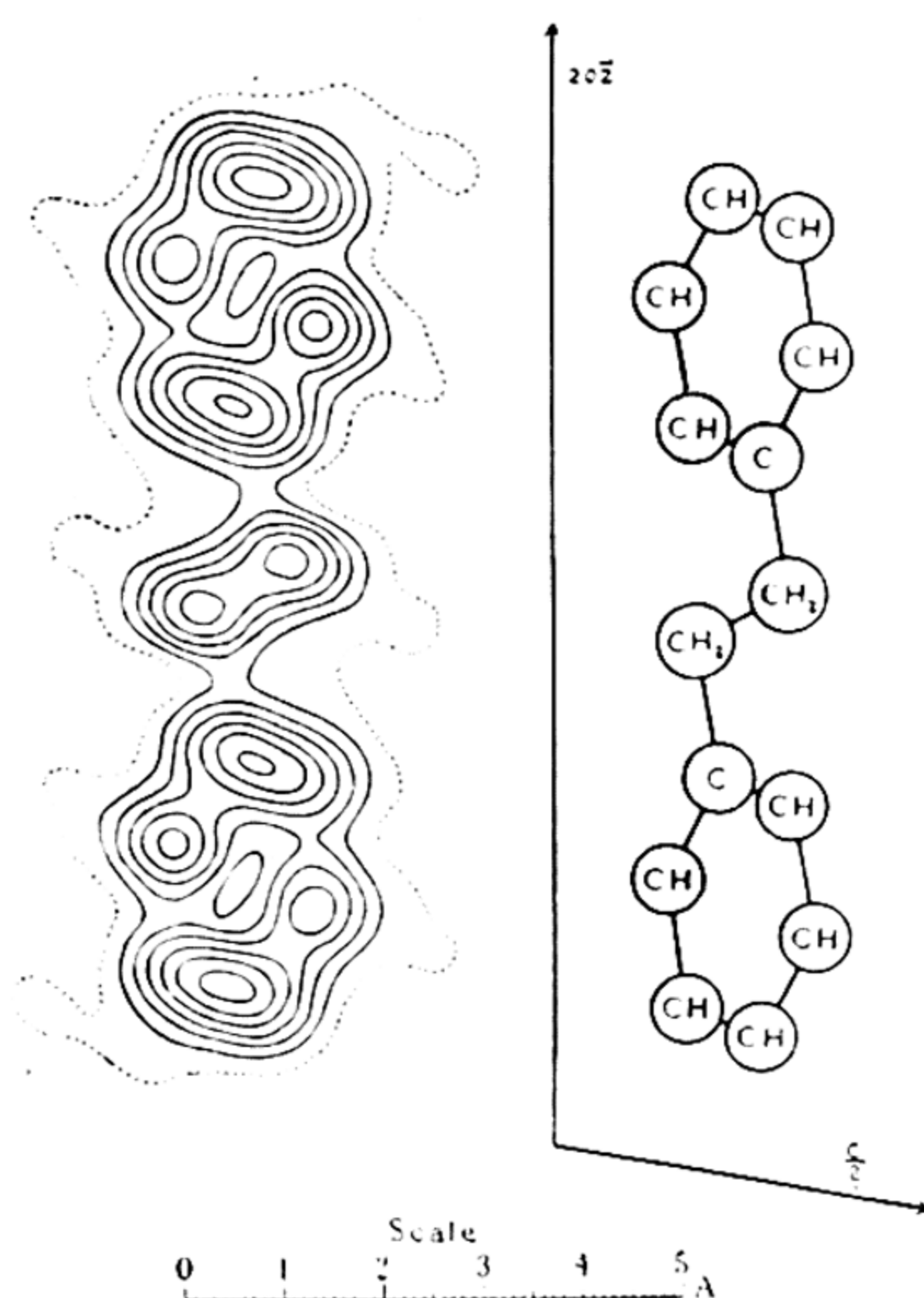
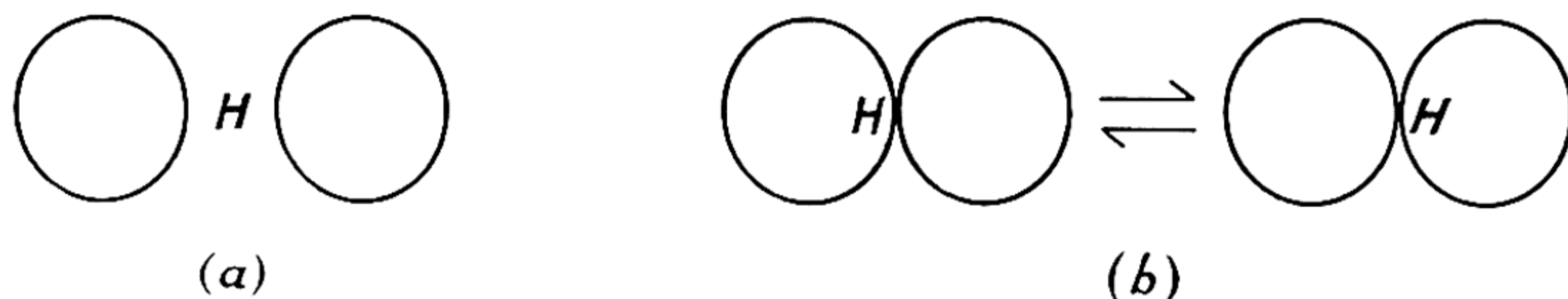


Figure 2. Dibenzyl projected along the b axis. It is found that the planes of the benzene rings are at right angles to the plane containing the zig-zag of the connecting CH₂ groups. The complete structure determination requires other projections at right angles to this one.

DISCUSSION

J. D. BERNAL. The study of the nature of the interatomic bond in the solid state can be approached in a different way, viz. by studying the transitions from ionic binding to homopolar linking on the one hand and to van der Waals forces on the other.

A most interesting case is that of bonds involving hydrogen. The simplest of these is the acid hydrogen bond found in solid and liquid acids and acid salts and even in gases, as in such bimolecular aggregates as $(\text{HCOOH})_2$. In this bond as studied by Huggins and Pauling, the H^+ ion may either be regarded as an ion with two oxygen (or fluorine) ions co-ordinated with it as in the left-hand figure,



or as a degenerate system resonating between the states shown on the right. In any case there is a very definite binding energy as is shown by the reduction of the effective radius of the oxygen atom to 1.27 \AA . as against 1.34 for the O^{--} ion and 1.8 for the neutral Ne atom.

I have recently been studying, together with Miss Megaw, another type of bond—that occurring in alkali and amphoteric hydroxides, which may be called the hydroxyl bond. The analysis of the crystal structures of the main groups of hydroxides (with the important exceptions of those of Na and K) has enabled us to follow the changes that the hydroxyl group undergoes in different ionic environments. The determining factor appears to be the electric field to which the hydroxyl ion is subjected, determined by the size and charge of the metallic cation, i.e., in Goldschmidt's terms, by its polarizing power. The extremes are the low fields of the weakly polarizing alkali ions where the ion behaves essentially like a fluorine ion, and the high fields and strong polarizing power of B^{3+} or Te^{6+} where the binding of the cation to oxygen approximates to the homopolar force of the oxyacids, while the hydrogen becomes correspondingly loosely bound.

The nature of the change can be followed quantitatively by the measurement of the distance between the hydroxyl groups attached to different cations. The values are given below:

Cation	Li'	Ca''	Mg''	Mn''	Fe''	Zn''	Al'''	Te ⁶⁺	B'''
Half distance between OH groups	1.80	1.88	1.61	1.56	1.53	1.41	1.39	1.38	1.35

There is an approximately linear relation between the logarithm of the interatomic distance and the energy of the cation hydroxyl bond. If we attempt to form a theoretical picture in wave mechanical terms it appears as a successive loss of degeneracy of the hydroxyl group with increasing fields. Free hydroxyl must have cylindrically symmetrical eigenfunctions. This is also probably its condition in the alkali hydroxides. With higher fields the tendency will be for the eigenfunctions to

split up into a tetrahedral configuration of a general methane-like character, though here only one of the concentrations of negative electricity will be occupied by a hydrogen ion. In the case of the intermediate bivalent hydroxides the three negative concentrations will be opposite the three cations, so that there is no essential difference from the case of a cylindrical group. In aluminium hydroxide only two of the negative concentrations are occupied by Al^{3+} ions and the remaining concentration can link with a hydrogen atom contained in a neighbouring hydroxyl group. This is the true hydroxyl bond, and it is significant that it gives the same interatomic distance 2.76 \AA . as that found in ice and water. With boron, sulphur and tellurium hydroxides it is not certain whether one or two negative concentrations are attached to a cation, as here the binding must be essentially homopolar, but in any case one negative place is left for the reception of the H^+ of a neighbouring hydroxyl group. The case of the neutral hydroxyl of the alcohols which exhibits marked hydroxylic binding must lie between these weak acids and the amphoteric hydroxides.

The relative weakness of the hydroxyl bond compared to the H bond is due to the presence of another H^+ in the neighbouring OH group.

This semi-classical picture has served to interpret and even to predict quantitatively the crystal structure and properties of hydroxides, and it would be very interesting to see if it could be given a stricter quantum theoretical basis.

Prof. P. P. EWALD. Most measurements give a test of the wave-mechanical theory of molecules or of crystals by checking the energy values rather than the actual ψ -functions or the electronic distributions. There is, however, one case in which a test of the latter presents itself: in the case of diamond. The diamond structure was established by Sir William Bragg in 1913 chiefly by help of the missing second order octahedral reflection (222). Later, this reflection, though very faint, was found to exist. It is a direct evidence for a difference of orientation of the carbon atoms forming the two interpenetrating face-centred lattices, of which the diamond lattice is composed. Or, to put it in another way, this reflection shows that the carbon atoms cannot be spherical or contain a centre of symmetry.

Dr Hönl and I have been trying to apply to the case of diamond the methods used by Slater and Pauling for calculating directed valency bonds. We start with a tetrahedral ground state of the carbon atom which consists of a combination of one $2s$ and three $2p$ electrons. We have, so far, neglected all but the 4 nearest neighbours and have not gone beyond the zero order approximation. Where the eigenfunctions of neighbouring atoms overlap, an induced probability for the presence of electrons appears. Integration of the total amount of charge thus accumulated round the centre of the lines joining the nearest carbon atoms gives about 0.8 electrons round each centre. The L shell of each carbon is consequently weakened to contain $4 - 4 \times \frac{1}{2} \times 0.8 = 2.4$ electrons only. It is possible, in an approximate way, to determine the Fourier expressions for the electron density in the unit cell of diamond. This gives the following Fourier coefficients (preliminary values!):

Order	(111)	(220)	(222)	(400)	(444)	(622)
Coefficient $ A $	15.6	19.6	0.24	12.7	9.6	$\sim 3.5 \cdot 10^{-7}$

The intensities to be observed by X-rays may be taken as proportional to $|A|$ and would thus lead to the ratio $(111):(222) \sim 100:1.6$, whereas the measurements of Sir William Bragg (after taking account of the angular functions) lead to $(111):(222) \sim 100:4$.

It is thus highly probable that the (222)-reflection of diamond can be accounted for quantitatively by the tetrahedral deformation of the C-atoms and that an accurate Fourier determination of the lattice will show further details of this most important case of an unspherical atom.

Dr A. MÜLLER. The problem of cohesion in organic solids resolves itself quite naturally into two parts. The first is the formation of the molecule from its constituent atoms. The paper¹⁰ by Heitler and London on the homopolar bond in the hydrogen molecule marks a fresh stage in the development of theoretical chemistry.

The second part of the cohesion problem deals with the interaction between the whole molecules in an organic crystal. Here the theory of Eisenschitz and London on the van der Waals forces has opened up new possibilities for the interpretation of crystal properties.

In a subsequent paper London has made a particularly interesting application of this theory. He calculates the heat of sublimation of a number of crystals from optical data of the constituent atoms and the lattice dimensions of the crystals. One of the crystals is solid methane.

In this paper London confines himself to molecules which in the simplified calculation are to be regarded as points.

Considering the extreme importance of the cohesion problem it seems most desirable to extend these calculations to crystals the constituent molecules of which cannot be treated as points. The theory in its general form is not restricted to point-like molecules. The correct application to an extended molecule is practically out of the question; an approximate calculation, however, can be made under certain conditions.

I have made such an attempt and have calculated the van der Waals potential of a paraffin crystal. These calculations are tedious and the paraffin crystal was chosen for its obviously simple structure. The calculated values for the potential are found to be larger than the observed heat of sublimation. This is to be expected, for it must be remembered that the potential due to the repulsion forces has to be subtracted from the van der Waals potential.

The van der Waals potential is found to be 2.4 kg. cal. per CH_2 gm. mol. if the CH_2 groups are taken as points lying along the chain axes, and 3.7 kg. cal. per CH_2 if the potential is calculated taking the nuclei of the C and H atoms separately in their correct position in the lattice. A calculation in which the centres are in the middle of the bonds gives an intermediate figure. The potentials are calculated for the crystal at room temperature. The observed value of the heat of sublimation is 2.1 kg. cal. per CH_2 gm. mol. How much the calculated values will be reduced by the repulsive potential cannot be stated; it is not to be expected that it will make much

difference. The calculations can be regarded as confirming the theory within the limits which may reasonably be expected in this approximate treatment.

Prof. J. C. SLATER. Professors Hückel and Hund have pointed out the two methods which have been used for computing interatomic forces, the first depending on electron pairs, the second on molecular orbitals, and have indicated that the second gives results in better agreement with experiment. I wish to state that I am in entire agreement with this conclusion, and that I believe that the second method, in the approximation to which it can be conveniently carried, is better than the first in a corresponding approximation. As a matter of fact, most of the calculations made by the Heitler and London method of electron pairs have neglected so many terms, in the nature of interaction integrals between three or more wave functions, lack of orthogonality, etc., which we know by the work of Coolidge on the water molecule to be large, that they possess practically no theoretical significance. The calculations of Pauling, for instance, seem to make quite unwarranted use of the theory. But the very fact that it is so difficult to include these missing terms is a strong practical argument against the Heitler and London method.

I believe, however, that the probable future development of the theory will not lie exactly along the lines of either of these methods so far discussed. In a study of metals, the theory of which in some ways has advanced farther than that of other solids, it seems most convenient not to consider exchange or interaction integrals of the conventional type at all, and I believe these will become of less importance in the theory. Instead*, it seems more convenient to consider separately the total potential and kinetic energies of the crystal, in their dependence on the positions of the atoms, relating them by the virial theorem. For the potential energy, we do not need to know the complete eigenfunction for all electrons of the crystal, but merely, as one can see from the work of Fock, a two-electron probability function, giving the probability that simultaneously electron number one will be at one point of space with one spin, and that electron number two will be at a second point with a second spin. The two-electron function is required because the potential energy involves only terms depending on pairs of electrons. Similarly the kinetic energy demands a one-electron probability in momentum space. The two-electron probability just mentioned involves the correlation between the positions of electrons with the same or opposite spins, as resulting from the exclusion principle, and it is this in particular which the method of electron pairs was designed to give correctly. But it now appears possible to determine this density approximately, following a suggestion of Wigner and Seitz, from the method of molecular orbitals. It has in this way been possible for metals, and one may hope that it will be possible for other solids, to give a tolerably complete account of the energy relations, by a method much more closely related to that of molecular orbitals than that of electron pairs, and much easier to understand in a physical way than the previous theories.

* See J. C. Slater, *Rev. Mod. Phys.* (October, 1934).

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THE DEVIATIONS OF REAL CRYSTALS FROM
THE IDEAL LATTICE STRUCTURE

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THE MOSAIC TEXTURE OF ROCK SALT

BY P. P. EWALD AND M. RENNINGER

Stuttgart

ABSTRACT. An account of experimental work on crystals of rock salt, from which it is concluded that the mosaic texture is a property of individual crystals, and is not of necessity shared by all crystals of a given substance. X-ray examination showed differences, particularly in the integral reflecting power, between natural crystals, cleaved but untreated, and those prepared by the method of Kyropoulos, showing that the artificial crystal has no mosaic structure. Small areas were found agreeing with the perfect crystal in integrated reflection and in half-width.

Polishing of the surface of crystals from either source results in a value for the reflecting power characteristic of a mosaic texture.

Rock salt is stated in the literature to be a typical representative of the mosaic class of crystals—an assertion which presupposes that the mosaic character is invariably determined by the kind of crystal. An alternative to this is the hypothesis that the mosaic texture is not a general constitutional property but an individual one, i.e. that it is a property which results from the growth or deformation of individual crystal layers. This hypothesis must be the correct one, as is shown by the following measurements*.

Rock salt, which had been taken without special precautions from the melt, in quantities of several c.c., according to the method of Kyropoulos, was tested by the “Divergence method” and gave an astonishingly sharp image of the reflecting surface, although, on examination by optical reflection, large areas of the surface were not absolutely perfect, but seemed broken up into strips which were several mm. wide and made angles of several minutes of arc with each other. (“Lineages” in Buerger’s sense.) The reflecting properties of the surface were then investigated using $\text{CuK}\alpha$ radiation for the $(1\bar{1})$ -position in a double spectrometer. The reflection curve obtained for two extensive regions of a pair of cleavage surfaces extended over an angular range of about $5'$. It consisted of irregularly distributed peaks, which were shown to correspond to the reflections from the individual disoriented crystallites.

In order to study the individual crystallites, an area of about $1\frac{1}{2} \times 3$ mm. of the second crystal was singled out by means of thin lead foil, so as to give a good reflection image of the goniometer slit by reflection. The reflection curve on the double spectrometer was obtained by fixing the first crystal and rotating the second in steps of $1''$. A bell-shaped curve resulted, having a half-width of $7.1''$ (half-width at half maximum). This is near the predicted theoretical half-width for an ideally

* For the full publication see M. Renninger, *Z. f. Kristall.* 89, 344 (1934).

absorbing crystal, which would be $5''$ according to the formula of Prins. The observed value of the half-width lies below all values of the half-width previously observed for rock salt by the double spectrometer, these being given as from $30''$ to $300''$. By interposing a diaphragm with a hole of 0.3 mm. diameter it was possible to test different portions of the $1\frac{1}{2} \times 3$ mm. area. In this way curves were obtained from different points, having sometimes secondary maxima which arise through reflections at adjoining areas or where there are inclusions. It may be that for the narrowest reflection curves of half-width $7.1''$, the difference from the theoretical value of $5''$ is determined by a flat folding of a few seconds in the cleavage plane, extending also through the nearly ideal region. It is also possible, however, that the somewhat too great width results from the small extension of the reflecting crystallites, which limits the interaction of the rays postulated in the dynamical theory of interference.

If a larger area of the crystal (of $30-50$ mm²) is used, the reflection curves from the separate points consist of an irregular series of peaks which for the artificial crystals are some $80-100''$ apart, while for the natural crystal they may cover about $1000''$.

If the reflecting surface is polished, some degree of smoothing of the reflection curve occurs together with a noticeable broadening of the half-width to some $1000''$ ($15'$).

The integrated reflecting power proves to be independent of the presence of the diaphragm—as would be expected from the fact that each element of surface gives its appropriate contribution. Nevertheless from the integral reflecting power we can decide whether the reflection is mainly produced as the sum of contributions from ideal reflecting elements, or whether it approaches another limiting case, that of the pure mosaic crystal of Darwin. For the mosaic crystal has always the greater reflecting power, and moreover there exists a difference in the dependence on angle. By measuring the integrated reflecting power in different orders it is possible to obtain a verdict as to whether the reflected beam results from the dynamical interference effect of coherent regions extending over at least 10^{-3} cm., or from the interference effect of mosaic crystals covering, at most, 10^{-4} cm.

It appears now that undisturbed cleavage surfaces of artificial rock salt produce integrated reflection curves which agree with the curve for the ideal crystal as well as can be expected. The departures amount to $+17$, $+6$, -8 per cent for the reflections (200), (400), (600), while the curve for the mosaic crystal is 4–5 times the observed value. This clearly proves that the reflection at these undisturbed artificial rock salt crystals arises predominantly from the ideal regions, and that only unimportant disturbances arise out of the mosaic blocks.

It is explicitly emphasized that in this comparison with the theory of dynamic interference, use is made of

- (1) The polarization factor $(1 + |\cos 2\theta|)$, instead of $(1 + \cos^2 2\theta)$ for the mosaic crystal.
- (2) The structure factor $|F|$ instead of its square $|F|^2$.
- (3) No separate determination of the effective absorption coefficient during reflection.

Moreover, the theoretical values are computed by means of

(a) Hartree's theoretical atomic factors, modified by a dispersion correction as given by Hönl on account of the relative closeness of the $\text{CuK}\alpha$ radiation to the chlorine absorption edge.

(b) The usual absorption coefficients of Jönsson.

(c) The refractive index according to the Lorentz dispersion formula.

(d) The Waller-Prins formula for the interference effect in an absorbing crystal.

(e) The Debye-Waller temperature factor as determined by James, Firth and Waller for rock salt.

The experimental values were reduced by

(α) Consideration of the polarization of the radiation incident on the second crystal due to reflection at the first crystal, and

(β) A correction on account of a small admixture of L radiation from tungsten, which was present in the primary beam, since this is reflected from the first crystal but not from the second.

Thus the dynamical theory in its best form at present has been used, and in it no values have had to be adjusted to fit the measurements.

In contrast to a freshly cleaved surface, the polished surface of the same artificial crystal gives an integrated reflection which agrees excellently with the curve for the mosaic crystal. The same values are obtained for a polished surface of natural rock salt. The values are some 4–5 times greater than the value given by an unpolished artificial cleavage specimen; they depart by less than 10 per cent from the values which are obtained from the usual formula for the mosaic crystal, when the secondary extinction is taken to have the same numerical value $g = 320$, as that given by Bragg, James and Bosanquet. We notice the fundamental difference which results from the polishing. Since the penetration of Cu radiation into NaCl is of the order of $\frac{1}{10}$ mm., the crystallites must be deformed, broken up and transformed into a mosaic right into the interior. Here there is still parallelism within about $\frac{1}{2}^\circ$ to the final surfaces, as may be seen from the breadth of the reflection curve ($\pm 1000''$).

A natural rock salt crystal from the Kochendorf mine on the Neckar, which when cleaved had an optically rather warped surface, was tested without being previously polished, using the good artificial crystal as a monochromator. Although the whole reflection-curve from a large area extended over a large angle, yet by using the diaphragm of 0.3 mm. diameter, peaks of moderate width—about 30–50"—were obtained from the individual crystallites. The integrated reflection values were intermediate between those of the perfect and of the pure mosaic crystal. Evidently the coherent areas of the natural crystal are much smaller than those of the artificial, or else there are broad layers with mosaic texture between the coherent areas.

We have in this investigation realized both limiting cases, as well as the transition from one to the other in the same rock salt—which clearly contradicts the conception of the mosaic as being a constitutional property. Of course, we are dealing here with the "röntgen mosaic," i.e. a mosaic having particles of less than

10^{-4} cm. For, in another order of magnitude, the optical (10^{-1} to 10^{-3} cm.), the artificial crystal is also not homogeneous, but a mosaic of crystallites. It is shown by this investigation that the coarser and finer mosaics are not inseparably connected but that either can be present or absent without the other.

INFLUENCE OF CRYSTAL IMPERFECTION ON INTEGRATED INTENSITY OF X-RAY REFLEXION			
(Rocksalt (400) reflex with copper K-radiation)			
Decreasing SIZE OF COHERENT DOMAINS ANGULAR DISPLACEMENT	1 sec.	1 to 10^3 sec.	Ord. of magnitude: degrees
10^{-2} cm RAYS <u>ABSORBED</u> IN SINGLE DOMAIN	Reflexion as for perfect crystal		
10^{-2} to 10^{-3} cm PARTIAL <u>TRANSMISSION</u> OF RAY THROUGH SINGLE DOMAIN			
10^{-3} to 10^{-4} cm PRIMARY EXTINCTION REDUCED BY SMALLNESS OF DOMAINS			
10^{-4} to $10^{-6.5}$ cm NO <u>PRIMARY EXTINCTION</u> LEFT.			
$<10^{-6.5}$ cm BROADENING OF REFLEX DUE TO SMALLNESS OF PARTICLES; <u>NO SECONDARY EXTINCTION</u> LEFT	Reflexion as for ideal mosaic crystal		

Primary extinction effective

Secondary extinction effective

Integrated reflexion as for perfect crystal

Integrated reflexion as for ideal mosaic crystal

There is another point we wish to make concerning the imperfections of crystals: it is of no use to speak, for example, of a mosaic structure in a general way. Our artificial crystal, though nearly perfect for X-ray reflections, was but a poor reflector for the beam from the goniometer and would not serve as a crystal for an X-ray spectrograph. In speaking of imperfections—as of every form of inhomogeneity—it is essential to state the scale applied, which varies according to the physical property considered.

From considerations of X-ray work it is thus possible to class the crystals into the table opposite, arranged first according to the *size* of coherent domains and secondly according to their *disorientation*.

It is ~~evident from~~ the table, for example, that for very small angular displacements the size of the coherent domains may vary much¹ more than for larger domains, without deviations of the reflecting power from that of a perfect crystal, whereas the ideal mosaic reflection will be obtained with larger particles if only their angular sweep is large enough.

As is shown by the regions in which the primary or the secondary extinctions or the mass absorption are effective, it is even necessary to state the wave-length used: if, instead of copper rays, molybdenum rays had been used for the measurements, the divisions of particle size would have been different from those given. This shows how careful one must be in interpreting the results of measurements of crystal imperfections.

For working out an actual case, it has been necessary to state in the table the wave-length and the order of interference. By changing these the divisions will shift, especially where mass absorption is concerned. But the whole arrangement of the table will remain unaltered and may thus be regarded as giving general information on the type of crystal imperfection open to X-ray investigation.

EXPERIMENTAL EVIDENCES OF GROUP PHENOMENA IN THE SOLID METALLIC STATE

BY ALEXANDER GOETZ

California Institute of Technology

ABSTRACT. The arguments in favour of some kind of superstructure in crystals are briefly mentioned, and it is explained that the word "group" is chosen to mean an agglomeration of a limited number of molecules in crystalline array, inside of which group the stability of a molecule is different from outside, and the size of which is a physical constant of the type of crystal under consideration. Thus a group structure neither accepts nor rejects the "secondary structure" dealt with by Zwicky.

The experimental evidence for the existence of groups is then reviewed.

Firstly, there is the evidence from etch figures on the cleavage planes of bismuth.

Secondly, there are phenomena at the transition from solid to liquid. Two observations here strengthen the case for a group structure, (a) the fact that the degree of super-cooling depends on the previous heating above the melting point, (b) the fact that the orientation of a crystal persists beyond the process of fusion, so that on subsequent solidification, the same orientation is found again. Again, the thermal e.m.f. of bismuth does not alter suddenly at the melting point, but changes gradually in a region of about 8° C. above the melting point.

Similar evidence is furnished by the behaviour of crystals formed partly within and partly without a magnetic field.

The third type of evidence is that from studying the distribution of the last traces of impurity. It would be expected that the foreign atoms would tend to segregate at the boundaries of the groups (a "surface" effect), and it is found in fact that there is a critical concentration where this changes to the more usual "volume" effect.

Finally, the comparison of the coefficient of expansion as measured macroscopically and by X-ray methods (which determine only the expansion inside the lattice, and ignore the boundaries) is discussed from the point of view of group phenomena.

It is the purpose of this paper to present a critical survey of experiments which can be interpreted as evidence of the existence of a higher periodicity in the crystal than the primary lattice structure. The discussion will be focused on experiments on metals, since the work of the author and his collaborators has been restricted to this field.

The need for an assumption of some kind of superstructure has originated from a large number of different fields of experience, e.g. the intensity of diffracted X-rays (Darwin), the anomalies of the tensile strength of crystals (Joffé, Smekal, Zwicky), phenomena of dissolving crystals (Traube and von Behren), etc. Accordingly, numerous theoretical attempts have been made to describe the nature of, and the reason for, the existence of such superstructures. As a consequence, the nomenclature is not uniform and, in order to avoid a confusion of terms, the word "group" has previously⁽¹⁾ been chosen by the author to designate an agglomeration of a

limited number of molecules in crystalline array, inside of which group the stability of a molecule is different from outside, and the size of which is a physical constant of the type of crystal under consideration. A "group phenomenon" is thus a quality of the crystal which can be described neither by assuming the crystal to present an infinite three-dimensional continuum nor by the assumption of more or less accidental discontinuities, as is represented for instance by the ordinary microscopically visible mosaic structure, characterized by measurable changes in orientation. On the other hand, the assumption that a crystal is an agglomeration of groups necessitates neither the acceptance nor the rejection of a "secondary structure" in the sense of Zwicky's theory.

This is not the place to discuss as a whole the different observations which make the assumption of a sub-division of a crystal necessary, especially since a number of very excellent treatises have been published recently^{(2,3)*}.

Considerable difficulty is encountered if we seek for experiments giving more than circumstantial evidence for the existence of such groups in a real crystal. The question must first of all be settled: What constitutes a periodicity in a crystal with a good alignment of groups of approximately equal size? Here the physical nature of the group boundary becomes of great importance and we are forced to assume that the physical conditions for the atoms at the surface of a group are different from those of the atoms inside. This seems to be especially important in the case of foreign atoms, which will cause a greater reduction in stability inside the group than at the surface. Hence we shall find such impurities in very small concentrations in an adsorbed state at the group boundary, and the foreign atoms will establish sources

* One trivial argument only may be pointed out which seems to speak rather definitely against the assumption of a crystal as a continuous repetition of the space lattice: the difficulty of producing large single crystals is a well-known experience; also, it is equally difficult, if not sometimes impossible, to prevent a substance from crystallizing in small crystals instead of remaining in an "amorphous" (i.e. non-crystalline) state. If the crystal were an ideal continuum, we should expect the minimum free energy of the N atoms available for crystallization to occur for a configuration in which they are all united in one large perfect crystal. The formation of a large number of small crystals would result in a larger free energy for the total system. In other words, the formation of one large crystal would be more probable than the formation of many small ones; at least it must be admitted, even if we make local fluctuations of conditions responsible for the occurrence of the large number of small crystals, that once a large crystal has been created, its disintegration into small crystals under external influences (gliding and twinning due to plastic deformation) should be a rare occurrence. Further, the reunion of the fragments into the large crystal by recrystallization should not only be possible but difficult to prevent. Experience shows, however, the opposite to be the case: first, it is sometimes exceedingly difficult to keep a large single crystal in this condition and prevent it from "aging" into mosaic conglomerates; second, once such disintegration has taken place, this process almost always proves irreversible under heat treatment. Since all this does not hold for crystals of small dimensions, we are led to assume that the above consideration is correct only for a limited value (\bar{N}) of N . ($N > \bar{N}$). In other words, if a crystal has reached a certain size containing \bar{N} atoms, the increase of stability of $\Delta N = (N - \bar{N})$ added atoms is small or zero, so that a further growth is less likely and it can even be more probable that the ΔN atoms (for a sufficient magnitude of ΔN) are more stable in the form of a new crystalline group which consequently reaches its maximum of stability after it in turn has grown to the content of \bar{N} other atoms. Thus a crystal would be true to its ideal definition only up to a certain size, and any real crystal of larger size would accordingly be a conglomerate of such elementary groups. It is easily seen that the stability of the whole system will not be influenced much by a slightly distorted arrangement of the conglomerate, which distortion will thus be probable. This argument, however, does not necessitate the presence of such distortions if, for instance, the conditions of growth are sufficiently well regulated and impurities absent, etc. The existence of large crystals with a high perfection in their goniometric relations is thus no fundamental argument against this concept.

of potential discontinuity throughout the crystal*. The experimental evidence for the existence of such periodically repeated discontinuities would thus be obtained if it could be shown that the length of the period indicated by the distance of such potential walls was independent of the concentrations of the foreign atoms within certain limits. Such a finding would also prove that this type of precipitation of the foreign component is fundamentally different from the well-known accumulation of impurities (segregation) in certain regions of the crystal at high concentrations⁽⁴⁾. It may be mentioned here that we believe we have found experimental evidence for the invariance of the length of the period when the concentration changes about tenfold.

To render these discontinuities visible and accessible to measurement, the author initially used the chemical method, etching cleavage planes of bismuth crystals and observing the size and the formation of the etch pits under the microscope, correlating it at the same time with an equidistant line-pattern constructed by means of an Abbé mirror⁽⁵⁾. In addition, a system of equidistant lines indicating the threefold symmetry on the (111) plane of such crystals, was observed before etching took place.

The validity of the interpretation of these experiments as proving the existence of a higher periodicity in the crystal has met with various criticisms, e.g.⁽⁶⁾ culminating in the suggestion that the source of the lines on the unetched plane represented some kind of plastic deformation affected by cleavage, and that the uniformity in the size of the etched figures was not sufficient to justify the assumption of a definite elementary unit (primitive perfect etch pit). These objections can be met in the following way: although the regions in which the line structures on the cleavage planes occur are the ones that look most perfect, and inspection of these regions under reflected polarized light does not give any indication of twin lamellae or other crystallographic discontinuities in the usual sense, no definite statement about the nature of such lines can be made owing to lack of means for investigating it. Their nature seems, however, to be of secondary importance to their occurrence at periodic intervals and the fact that the length of the period was found to be independent of the individual crystal. It has also been claimed⁽⁶⁾ that the observed regularity was not a "*real*" but a "*pseudo*" *regularity*, especially in view of the fairly large margin of error of the microscopic observation caused by the closeness to the optical resolving limit. Against this the following general argument may be advanced: such a distinction presupposes a distinction between regularity and pseudo-regularity and does not seem to be justified. Considering the normal conditions of growth of a crystal, and the magnitude of the groups concerned, we should expect fluctuations in size which would render a perfect regularity impossible. In other words, the existence of a regularity *per se* seems to be established as long as a sufficiently large number of observations have been taken and a statistical distribution crowding around *one* value is found; the broadness of the distribution only

* At this point it may be mentioned that it would be misleading to ascribe the existence of such structure only to the accident of the presence of impurities. This would seemingly be the same as ascribing the inner structure of an organic cell to the presence of a dye. Furthermore most crystals with which we have to deal are grown under such conditions that the complete absence of foreign atoms cannot be realized, and there is evidence that, even if the substance is of extreme high chemical purity, adsorbed gases may furnish the disturbing atoms.

renders the absolute value of the length of a period more or less uncertain, but does not affect the validity of the assumption that a periodicity exists. It thus seems that the situation is vastly different as between a Gaussian distribution, however broad, and a complete randomness: in the former case *we can evaluate finally a definite physical constant* characterizing the crystal (not the individual crystal) under consideration and we have to find a mechanism of crystal formation which can account for the occurrence and magnitude of this constant; in the latter case, the whole phenomena are attributed to mere accident. Thus, arguing along these lines it seems unjustified to establish a difference in principle between perfect and pseudo-regularity.

It is to be expected that the existence of groups would result in a great number of phenomena which should be accessible to experiment, in addition to visual observation under the microscope, this being at the same time the most direct method, and also the one most open to criticism.

As far as metals are concerned, the further (experimental) evidence so far available divides itself into observations at the transition from the liquid into the solid state and *vice versa*, and into certain properties of the crystal in the solid state. The subject will be treated accordingly in this order.

Concerning the transition from one phase into the other, there exist two seemingly important phenomena which yield evidence against the general assumption that a crystal loses its structure on passing through the melting point and, in our opinion, in favour of the hypothesis that the formation of groups antecedes the formation of the solid crystal: one is the observation of the dependence of the degree of supercooling upon the previous heating of the melt above the melting point, the other the persistence of the orientation of a crystal beyond the process of fusion.

Webster⁽⁷⁾ has shown that for bismuth, lead and tin, the liability of the melt to supercool is larger, the more the melt has been superheated (heated above the melting point) previously. As far as metals are concerned, the observed differences were unusually large: it was possible to supercool bismuth to 40° by superheating the melt 80° , whereas superheating for only a few degrees permitted but a few degrees supercooling*. It is obvious that the dependence of the degree of supercooling upon the thermal history cannot be reconciled with the idea that the crystal builds itself from single individual molecules out of the melt, since the kinetics of the molecules in the liquid and their interaction cannot depend on the degree to which the liquid had been heated previously.

With regard to the process of melting, the author has first observed in bismuth crystals⁽⁸⁾ that the orientation as well as the microscopic properties of the individual crystal (regions of different orientation, twin lamellae) are preserved in the melt for several degrees above the melting point, as is indicated by their reappearance if the melt is kept from mechanical disturbance and recrystallized into a single crystal. These observations on "latent" crystals have recently been confirmed independently⁽⁹⁾. The fact that the capacity of a molten single crystal for accepting an orientation different from its previous one on inoculation with a new seed crystal

* The author found recently that pure gallium shares this property to a remarkable extent.

depends on the degree to which it was previously superheated, points in the same direction. Similar phenomena are well known to occur for liquid crystalline substances at the transition from the solid into the smectic state⁽¹⁰⁾.

Very little material is available concerning the degree of abruptness with which the physical qualities of a crystal, characteristic of its solid state, disappear when fusion sets in. The nature of the phenomena to be expected is such that one would think them most likely to be overlooked if no special care were taken to keep the crystal "latent". Only the experiments of Soroos⁽¹¹⁾, concerning the disappearance of the thermo-electric e.m.f. of bismuth crystals, strengthen the assumption that the configuration which causes this property to be different from that for the liquid state survives the fusion to a certain extent for several degrees. He found that the e.m.f. characteristic of the solid crystal does not change discontinuously into the e.m.f. of the liquid but that this transition is gradual and is spread over a temperature range up to 8° above the melting point.

Into the same group fall experiments which deal with the possibility of changing the physical properties of an anisotropic metal by studying its crystallization in a magnetic field. It has been known for a long time that under such circumstances these crystals show an orientation in which the most paramagnetic direction of the crystal is oriented parallel to the lines of force of the magnetic field^(12, 13). In recent years we^(14, 15) have tried to study such phenomena under more controlled conditions, and it was found that it is actually possible to obtain single crystals with different properties (thermal e.m.f., electric conductivity, density) if one half of the crystal is grown within, and the other outside the magnetic field, although the external appearance does not show any crystallographic difference between the two halves. Also this indicates that the crystal must have existed before it became rigid, since a directional effect upon the crystal can only be impressed upon it by a magnetic field if an anisotropy exists which cannot be present in a liquid in which all the molecules are free to move independently of each other. The objection⁽¹⁶⁾ that the difference can be ascribed to some kind of plastic deformation caused by the ponderomotive forces of the magnetic field can be met, however, by the argument that the absolute values of the susceptibility are so small that, within the range of fields used, the forces must remain far below the elastic limit of the crystal near the melting point. Thus it only seems possible to assume a plastic deformation of the liquid, i.e., of the groups before they reach the rigid state. Again, we have here a direct analogy with the behaviour of paracrystalline liquids, where it has been shown⁽¹⁷⁾ that the alignment of the molecular swarms can be influenced in a similar way by a magnetic field.

The chief experimental evidence against the existence of such groups in the immediate neighbourhood of the melting point was the fact that it was impossible to obtain X-ray patterns which indicated more regularity than the usual statistical arrangement of molecules. The following arguments, though, can be brought against the validity of such evidence: it is known that the geometric arrangement of most metals in the solid state is that of a statistical—close packed—agglomeration of atoms, which varies in general only very little from the ideal configuration of packing for spherical molecules. We should thus not expect to find a large change even if the

atoms were agglomerated in some form of paracrystalline configuration. An exception of course is formed by metals which in their solid state differ largely from the statistical arrangement, such as bismuth, arsenic, antimony, gallium, tin, indium, etc., and it has actually been found for tin and gallium that close to the melting point, the intensity distribution for the molten metal differs from that indicating the simple statistical distribution. In the case of gallium the periodicity was found to fit even better with the structure of the solid state^{(18, 19)*}. Unfortunately there is no experimental material available yet for molten anisotropic metals close to the melting point, except those mentioned.

Summarizing this set of phenomena, it can be said that they necessitate the assumption of a persistence of the crystalline structure beyond the fusion of the crystal, which in turn necessitates the assumption that a crystal cannot be formed without the preceding formation of such paracrystalline agglomerations. However, the material is exceedingly scarce and the evidence can certainly not yet be called conclusive.

On account of the greater accessibility and the seemingly more general interest, our efforts have mostly been directed towards tracing group phenomena in the solid state. As has been discussed at the beginning of this paper, the effect of the last traces of impurities in small concentrations proves to be of assistance, in a similar way to the dye in biological microscopy. Two conditions have to be fulfilled, viz. the impurity must be soluble within the range of concentration used, and the concentration must be so small that a volume effect is not noticeable (i.e. 1 : 100 to 1 : 40,000). As indications for the effect of foreign atoms in bismuth crystals, we chose the magnetic susceptibility, the conductivity and the thermoelectric e.m.f. Several hundred crystals were grown and several thousand observations were taken of the susceptibility in different directions in the crystal in the range from liquid air temperature to the melting point, as a function of the concentration of the impurity and of its relative difference in the electron configuration to the bismuth atom⁽²⁰⁾. From the standpoint of group phenomena, the interesting result is that we find a *critical concentration* of the admixture, below which the specific effect of the foreign atom is from ten to one hundred times larger (depending on temperature and type of impurity) than above. This apparently has to be interpreted as an indication that below the critical concentration we are dealing with a surface effect, whereas for higher concentrations the usual volume effect sets in. The authors have thus suggested that the foreign atom is absorbed at the internal surface of the crystal and that the critical concentration is reached when the internal surface is saturated, i.e. when, according to the picture outlined above, the group boundary is populated by foreigners to such an extent that the loss of stability caused by a further insertion of foreigners into the boundary equals or exceeds that due to absorption into the volume of the group. According to expectation, the critical concentration is exceedingly well defined at low temperatures, and its value proves to be reproducible and independent of the conditions of growth of the crystal within the available variations. The values for the critical concentrations were found to be: ca. 0.09 per cent atoms

* The author found recently that pure gallium shares this property to a remarkable extent.

for tellurium, 0.3 per cent for tin, 0.9 per cent for lead and selenium. It is seen that these concentrations are not only far below the limit of volume solubility as indicated in the phase diagram, but also that there exists a proportionality between the critical concentration of an element and its saturation in the crystal, e.g. the phase diagram indicates that the solubility of tin in bismuth is approximately one-third of that of lead in bismuth (1.7 and 5.3 per cent) and the same ratio prevails between the respective critical concentrations. Since the volume solubility of a foreign atom in a crystal can be taken as a measure of the increase of total free energy of the crystal on the insertion of the foreign component, a similar respective increase will be effected by the adsorption at the group boundary; thus, for instance, one tin atom will cause as much disturbance in the boundary as three lead atoms, and consequently the critical concentration of tin will be one-third that of lead. If the group boundary is thus saturated, the effect upon the crystal is perfectly definite and there is no possibility of deciding from the physical properties of the crystal whether it contains tin as foreign admixture or lead in three times the concentration. The existence of such a critical concentration points definitely towards the existence of groups of approximately equal size, especially since the volume of the groups calculated under the assumption of a monomolecular population of the group boundary by foreigners at the critical concentration, proves to be of the same order of magnitude as the one calculated from the above mentioned experiments on primary etch pits. It amounts to 10^{-14} to 10^{-15} cm³. The complexity of these phenomena is greatly increased by the fact that foreigners such as tin, which are left-hand neighbours to the crystal atom (bismuth) in the periodic system, affect the crystal in a crystallographic direction opposite to the right-hand neighbours, e.g. tellurium to bismuth. For such details reference must be made to the original publication⁽²⁰⁾. Measurements on the localization of traces of polonium dissolved in bismuth crystals⁽²¹⁾ support this point of view inasmuch as a distinct statistical crowding around a definite distance (0.54μ) between the loci of high polonium concentration along [111] was found which is in excellent agreement with the distance of the (111) layers measured microscopically.

If the group boundary is the locus for a disturbance of the continuity of the space lattice, we should expect it to affect the thermal dilatation of a crystal in a way which is accessible to experiment. It is known that the thermal dilatation is definitely a co-operative phenomenon, i.e. that to produce a large thermal expansion it is necessary to have a large number of atoms in good geometric configuration, whereas a disturbance of this array will cut down the expansion accordingly. We should therefore expect that the region across the group boundary would not contribute to the thermal expansion of the whole crystal, especially at higher temperatures in the presence of impurities, since here the region of disturbance will penetrate far into the individual group. If we thus compare the thermal dilatation measured with a sensitive dilatometer over the whole length of the crystal, with the increase of the lattice parameter, the temperature coefficients should be systematically different, since the disturbed regions are not recorded by the X-rays, whereas the dilatometer integrates over the crystal as a whole. Thus the lattice expansion should come out to be larger than the integral expansion. The first measurements of this

kind were performed in our laboratory^(22, 23) on bismuth crystals containing 0.1 per cent impurities and a very large divergence was found between the two kinds of dilatation; later, Jay⁽²⁴⁾ determined the thermal expansion by the powder method on very pure material and came to the conclusion that this divergence was very small if it existed at all. In continuation of the original experiment our previous results were checked during the last few years with more refined methods, especially with regard to the integral expansion, and the exact quantitative analysis of the content of foreign atoms in the crystal^(25, 26). A partial agreement with Jay's results could be obtained inasmuch as it was found that for very pure material (99.998 per cent or better) the divergence mentioned disappears for high temperatures owing to a change of the macroscopic (integral) expansion. This indicates clearly that the disturbance by impurities must take place in discrete regions of the crystal and not in the volume. The present experimental material seems to justify the assumption that it is *not* possible to affect the lattice expansion by the insertion of foreign atoms in concentrations of the order of the critical concentration. For the details also in this case, reference must be made to the original publications.

Another way of approaching the nature of group phenomena experimentally has already been indicated. If the stability of a crystal depends on its size, in the sense that a crystalline agglomerate of a small number of molecules ($N \leq \bar{N}$) has a stability different from a crystalline agglomerate containing a larger number of molecules ($N \geq \bar{N}$), we should expect certain types of physical properties of the crystal to become dependent on the size of the crystal as soon as its magnitude exceeds the critical magnitude ($N = \bar{N}$). It is obvious that these types of property would be identical with those affected by the insertion of foreign atoms in the crystal, e.g. the crystal diamagnetism, conductivity, Peltier effect, integral expansion. On account of experimental difficulties, only the susceptibility has been investigated so far, and during the last three years, methods have been developed at our laboratories to render the measurement of such qualities accessible to experiment. The early work in this field performed in India^(27, 28) has already given clear indication that the susceptibility of colloidal suspensions of graphite, bismuth and antimony becomes definitely dependent on size when the particle size becomes of the order of 10^{-4} cm. One of the main sources of error in the exact determination of this size function lies in the anisotropic qualities, and the large error which results from measuring with a large number of particles which, owing to their non-spherical shape, arrange themselves according to a statistical law. We have avoided this difficulty by producing suspensions of crystalline particles in which the particles are all fixed in a crystallographically parallel position to each other, so that their physical properties can be measured in different directions with respect to their crystal orientation^(29, 30, 31). The principal difficulty in these experiments lies in the exact determination of the size function: if the dependence on size were caused by a surface effect (e.g. adsorption of paramagnetic O_2 in case of a diamagnetic susceptibility of the crystal), the size function should follow a hyperbolic law, since the diamagnetism should then decrease inversely proportional to the diameter of the particle, whereas the existence of a critical size should be indicated under sufficiently controlled experimental

conditions by a curve which approaches a pronounced break when this magnitude is reached. The experiments of the Indian authors so far indicate a hyperbolic function, whereas our results on very carefully purified material and a small margin of particle size, point definitely towards a larger change in the size function in the critical region than can be described by an hyperbola. It could be proved especially that there is no dependence on size for particles above 5×10^{-4} cm. diameter.

A crucial experiment to decide between a mere accidental surface phenomenon and an innate property of the crystal is seen in the measurement of these properties at different temperatures, especially in the lower temperature region, since it is to be expected that surface adsorption would change the size function considerably with temperature, whereas the size of the group should obviously stay unaltered. Experiments of this kind are in progress but have not yet yielded definite results.

In conclusion, the picture derived from the group hypothesis may be recapitulated: Before entering the solid state in crystalline form, a metal has to go through a paracrystalline interphase in which molecular groups are formed, inside which the geometric configuration is already close to that of the solid lattice. The size of these groups is a physical constant of the crystal and lies between 10^{-14} and 10^{-15} cm.³ The boundaries of these groups may give rise to discontinuities in the solid crystal. Furthermore, these boundaries form an internal surface of definite area in the large solid crystal, on which foreign atoms are adsorbed as long as their concentration is smaller than the concentration needed for saturating the surface. This concentration is called the critical one and is reflected in the concentration diagrams at low temperatures by a sharp decline of the specific influence of the foreign atom upon a number of physical qualities of the crystal. This critical concentration is a constant characteristic for any combination of totally or partially soluble metals.

Whereas it cannot be denied that the experimental support for this hypothesis is still very meagre and mostly of circumstantial nature, and that it is collected from metals generally considered to have unusual properties, it seems to us that already there exists sufficient material which does not lend itself to an interpretation along the traditional concepts of the formation and the constitution of a metallic crystal. The attempt to interpret this material by means of the above hypothesis is admittedly primitive and in many ways much less detailed than other attempts to describe discontinuities in non-metallic crystal lattices. It is also probable (even most likely) that a good deal of the elements of this hypothesis can be found in the theories of other authors. The justification of this exposition should thus be seen only in the attempt to point out a number of experimental results and to describe them as consistent with the picture to the composition of which a minimum of purely hypothetical material had to be used.

REFERENCES

- (1) A. GOETZ. *Z. f. Kristall. Sonderheft* (1934).
- (2) A. SMEKAL. *Handb. d. Phys.* **24**, 2 (1933).
- (3) F. ZWICKY. *Rev. Mod. Phys.* **6**, 193 (1934).
- (4) M. STRAUMANIS. *Z. f. anorg. Chem.* **180**, 1 (1929).

- (5) A. GOETZ. *Proc. Nat. Acad.* **16**, 99 (1930).
- (6) M. J. BUERGER. *Z. f. Kristall. Sonderheft* (1934).
- (7) W. L. WEBSTER. *Proc. Roy. Soc. A*, **140**, 653 (1933).
- (8) A. GOETZ. *Phys. Rev.* **35**, 193 (1930).
- (9) E. DONAT and A. STIERSTADT. *Ann. d. Phys.* **17**, 897 (1933).
- (10) W. BRAGG. "Liquid Crystals." *Roy. Inst. Gr. Brit.* (Nov. 1933).
- (11) A. SOROOS. *Phys. Rev.* **41**, 516 (1932).
- (12) S. PLÜCKER. *Pogg. Ann.* **76**, 583 (1849).
- (13) M. A. LEDUC. *C. R.* **140**, 1022 (1905).
- (14) A. GOETZ and M. F. HASLER. *Phys. Rev.* **36**, 1752 (1930).
- (15) A. GOETZ and A. B. FOCKE. *Phys. Rev.* **37**, 1044 (1931).
- (16) H. E. BUCKLEY. *Z. f. Kristall. Sonderheft* (1934).
- (17) H. ZOCHER. *Rep. Far. Soc.* p. 945 (1933).
- (18) F. SAUERWALD and W. TESKE. *Z. f. anorg. Chem.* **210**, 247 (1933).
- (19) H. MENKE. *Phys. Z.* **33**, 393 (1932).
- (20) A. GOETZ and A. B. FOCKE. *Phys. Rev.* **45**, 170 (1934).
- (21) A. B. FOCKE. *Phys. Rev.* **45**, 219 (1934); **46**, 623 (1934).
- (22) A. GOETZ and R. C. HERGENROTHER. *Phys. Rev.* **40**, 643 (1932).
- (23) T. L. HO and A. GOETZ. *Phys. Rev.* **43**, 213 (1933).
- (24) A. H. JAY. *Proc. Roy. Soc. A*, **142**, 237 (1933).
- (25) J. W. BUCHTA and A. GOETZ. *Phys. Rev.* (In press 1934.)
- (26) R. B. JACOBS and A. GOETZ. *Phys. Rev.* **47**, 94 (1935).
- (27) V. J. VAIDYANATHAN. *Ind. J. Phys.* **5**, 559 (1930).
- (28) S. R. RAO. *Ind. J. Phys.* **6**, 241 (1931).
- (29) A. GOETZ, A. B. FOCKE and A. FAESSLER. *Phys. Rev.* **39**, 169, 553 (1932).
- (30) A. GOETZ and A. FAESSLER. *Phys. Rev.* **40**, 1053 (1932).
- (31) A. GOETZ. *Phys. Rev.* **45**, 282 (1934).

ON THE CAUSE OF THE LOW VALUE OF MECHANICAL STRENGTH

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ABSTRACT. The discrepancy of the order of 500 times between the theoretical values of tensile strength and the values normally observed is recalled, and it is pointed out that amorphous substances show a similar discrepancy.

Two kinds of rupture are distinguished: (1) plastic rupture, in which there is a reduction of area at some point before fracture occurs; (2) brittle rupture.

The influence of plastic deformation on strength is then considered in some detail.

Brittleness occurs if the elastic limit increased either by previous plastic deformation or by lowering of temperature reaches the practical tensile strength. Two types of explanation have been put forward to account for this: (a) internal faults and (b) surface crevices.

Many experiments proving the importance of surface conditions are next described, among them that of dissolving the surface of rock-salt in hot water during the loading experiment; this raised the strength twenty times.

The conclusion reached is that the practical weakness is due essentially to the sharp discontinuities present on the surface.

§ 1. TENSILE STRENGTH AND MOLECULAR COHESION

TENSILE strength may be regarded as a measure of the molecular forces holding a material together. However, it is well known that the mechanical strength is usually many thousand times lower than would be expected from the theory of crystal lattices. This disagreement is easily explained by a closer examination of the mechanism of rupture. The local stress at the region where rupture takes place is always many times greater than the mean value over the whole cross-section. The best evidence that this is the case is provided by the splendid experiments of Griffith on the influence of discontinuities on the tensile strength of glass.

There are various reasons for assuming that the real molecular cohesion greatly exceeds the average stress during rupture.

(1) There is the disagreement that exists between theoretical and practical values (for rock-salt 200 kg./mm² and 0.4 kg./mm²), while the ordinary lattice theory gives quite consistent results for the energy of the crystal.

(2) Rupture is often observed in that stress region where Hooke's law still obtains, while any theory of molecular forces would predict that the maximum stress leading to rupture would be reached gradually. The modulus of elasticity as a derivative of stress upon strain must reach zero value at the maximum value of the force of cohesion.

(3) While tensile strength has a definite value as measured by the usual method, it may change many-fold if the test conditions are altered. Measured in hot water, the strength of rock-salt increases from 0.4 to 10 kg./mm² (Joffé, Levitskaya and others); protected from surface crevices, the strength of glass increases ten times (Griffith); mica stretched in such a way that the edges remain stressless, increases in strength from 30 to 300 kg./mm² (Orowan). In all these cases only the surface conditions were specially selected, while nothing was changed in the interior of the body; the average atomic distance as determined from the density gave the usual value.

The problem of practical weakness of materials is not confined to crystal lattices. Amorphous glass shows the same discrepancy of practical weakness and theoretical strength and the same large influence of surface conditions. We shall however consider crystals in the first place.

§ 2. PLASTIC RUPTURE

It will be useful to distinguish two kinds of rupture, plastic and brittle. The first type is usually manifested by a reduction of area on some cross-section where final fracture occurs. The second type occurs without appreciable plastic deformation. We may obtain both kinds of rupture on the same material by varying the rate of loading.

The general case is the rupture of a crystal which has previously been deformed plastically. The elastic limit of a single crystal is very low. Kirpicheva, Levitskaya and myself first found, using X-ray methods, a value for rock-salt of 920 gm./mm² at room temperature, decreasing at the melting point (800° C.) to zero. At this stress of 920 gm./mm² we observed a change in the Laue diagram. Every spot (except one) became double; at higher loads it became divided into a series of spots changing the Laue diagram into a system of "tails" instead of single spots. We stated then, that this limit corresponded to a flow of the crystal and not to the first change in the lattice. Measurement by a mechanical device reduced the observed value of the "elastic limit" to 200 gm./mm²; an optical method developed by Obreimov (the appearance of double refraction along the gliding planes) gave a still lower value of 70 gm./mm². By careful annealing of both pure artificial and natural crystals, Classen-Nekludova was able to observe the first fringe of double refraction at 9–10 gm./mm². The same value has been found by Podashevski using the change of photoelectric current produced by plastic deformation.

The elastic limit of carefully prepared single metallic crystals is equally low. It increases rapidly as plastic deformation proceeds up to the point where continuous flow commences. Our opinion, that a high elastic limit for shearing stresses is characteristic of a solid body and distinguishes it from a liquid, is founded on the study of glasses, polycrystalline materials and crystals which have been previously plastically deformed. A crystal lattice, as such, is characterized by a very low elastic limit.

When plastic deformation precedes rupture, the mechanical properties of the

crystal are thereby changed. We shall consider what influence the phenomenon of plastic deformation has on strength.

In 1918, Kirpicheva and myself* showed that the plastic deformation of a rock-salt crystal leads to distortion of the crystal lattice along definite crystalline planes. By slipping and twinning on these planes, the crystal becomes divided into a large number of pieces, neighbouring pieces having relative orientations. Obreimov and Shubnikov†, using double refraction methods, have measured the stresses existing at the boundaries of the pieces and found tensile and compressive stresses, on opposite sides, of intensities up to 10 kg./mm². The pieces are thus in equilibrium (Masing‡). Investigating carefully the mechanism of such plastic deformation, Classen-Nekludova§ found the phenomenon of deformation (first observed by P. Ehrenfest and myself), to consist of multiples of unit shearing motions, each consisting of a large number of such unit slips. A theory of this phenomenon has recently been given by Orowan||.

Stepanov¶ suggested that the energy developed at a thin boundary layer during the short time occupied by a slip or "jump" ought, temporarily, to raise the temperature of the layer. He seems to have confirmed his assumption by the observation of a temporary increase of conductivity of rock-salt crystals along the gliding surface during a plastic deformation. If in other crystals the melting point was not reached, a considerable change of temperature manifested itself by the appearance of new high temperature manifestations such as annealing, recrystallisation, etc.

Thus plastic deformation possesses many features which tend to obscure the real strength which Stepanov assumes is developed at rupture.

(1) During the short period of slipping, the cohesion in the boundary layer involved is greatly reduced, possibly even to the value for the liquid state as given by the capillary constant. Discontinuities may be formed during this period, especially at higher temperatures near the melting point of the crystal.

(2) The sliding produces, inside the crystal and on its surface, discontinuities which may act as "crevices" and reduce the strength. This effect seems to be most important at average temperatures.

(3) Both layers adjacent to a boundary of a region of slip are left in a stretched or compressed state. Stresses much larger than the practical strength disappear at a rate which falls with decrease in temperature. They are added to the elastic stress produced by external forces and lead to a distortion of the crystal. Those stresses are especially dangerous at low temperatures.

Contrary to Stepanov's theory, we are accustomed to consider that plastic deformation increases tensile strength; but the influence is secondary. Plastic deformation increases the elastic limit mainly by a distortion of the regularity of the lattice. Up to a new enlarged limit no sliding occurs and therefore there is no chance for rupture. Increasing the amount of slip results in the production of

* *Phil. Mag.* 43, 204 (1922).

† *Erg. Exakt. Naturwiss.* 2, 206 (1923).

|| *Z. f. Phys.* 89, 634 (1934).

† *Z. f. Phys.* 41, 907 (1927).

§ *Z. f. Phys.* 55, 555 (1929).

¶ *Sow. Phys.* 2, 26 (1932).

increasingly large stresses and discontinuities until at some point (most probably on the surface) the theoretical strength limit is reached. The development of such a discontinuity leads then to rupture.

Amorphous bodies such as resins, glasses and varnishes do not show any influence of plastic flow, either on the elastic limit or on mechanical strength.

§ 3. BRITTLE RUPTURE

If the elastic limit increased by previous plastic deformation (rock-salt) or by lowering of temperature (quartz) reaches the value of the practical tensile strength, the material becomes brittle. Rupture occurs either without any plastic deformation or at the first sliding; the observed strength is, however, much lower than the theoretical value. Two different explanations have been proposed to explain this discrepancy: internal faults (Smekal's "Lockerstellen" and Zwicky's "secondary structure") and surface crevices (Griffith, Joffé). There is no doubt that some kind of internal faults may act in just the same way as surface crevices (less dangerous, however, because the concentrated edge stresses may be lowered by plastic flow of the material and changed to a more uniform distribution). Sharp edges of a crystal included in a metallic body will probably also decrease mechanical strength. However, whether or not irregularities are produced by heat motion during crystallization, the frequently observed mosaic structure of a crystal would have the opposite effect. As such irregularities render gliding on a crystalline plane more difficult, they increase the elastic limit and therefore ought to increase the strength.

In the case of rock-salt, two experiments were performed by Levitskaya and myself to demonstrate the importance of surface conditions. Dissolving the surface by hot water during the loading experiment, we found strengths exceeding the usual value by a factor of twenty or even more. Many objections were raised against the conclusion drawn from our experiment. Polanyi ascribed both the high strength and the exceedingly marked plasticity to a lowering of the elastic limit by water. But no change in the elastic limit was found on careful measurement. Smekal in his first paper on this subject, and later Barnes, assumed that the penetration of water inside the crystal through narrow canals makes the gliding easier and leads to an increase in strength. (Experiments carried out under Smekal's direction changed his opinion.) This assumption however is in contrast with our observation that a saturated solution of salt has no influence at all, while it is clear that the water inside the rock-salt crystal must be saturated in any case. A direct disproof of the water penetration explanation was given by Classen-Nekludova. She protected a small strip of the crystal by vaseline. Notwithstanding the fact that practically the whole surface, except the small strip, was dissolved to a large degree in hot water and the penetration of water in the crystal could, and probably did, proceed just as easily as without the protecting strip, the strength observed was the strength of a dry crystal. Thus it was shown that the smallest dry spot on the surface may be responsible for the practical weakness of the whole crystal.

In our second experiment we used a sphere of rock-salt cooled carefully at liquid air temperature and then suddenly plunged into hot water or into molten tin. (Grünberg's calculations of the distribution of heat and stress show that after 1–2 seconds the central part must be stretched by the heated outside layer, while the outside surface is still unstressed.)

Neglecting the plastic stretching of heated sheets, we should expect a uniform tensile stress of about 70 kg./mm² at the centre of the sphere. The plasticity of the warmer part will somewhat decrease this value, but it certainly exceeds the practical strength many times.

Still more conclusive are the experiments of Orowan on mica. Applying a tensile stress to the middle part of a plate of mica in such a way that the edges were practically unstressed, Orowan obtained values for tensile strength exceeding by ten times the strength obtained in the case where edges were involved. In a second experiment, Orowan observed that sheets of mica without crevices on the edges and giving a high strength, had a very low acoustical damping and emitted a clear sound. The same sheets with crevices on the edges gave a dull clang and had a low strength.

The influence of surface conditions was similarly found by Davidenkov and Wittmann on polycrystalline steel. Measured by a pendulum blow, they found a definite temperature (about -120°C.) where the brittle rupture changed to a plastic one. This transition point (which is the crossing point of the strength curve and the elastic limit curve as functions of temperature) decreased by 20°C. if the surface of the steel sample was polished or etched. It means that the tensile strength was increased by the removal of surface discontinuities.

The theory and well-known experiments of Griffith on glass also afford evidence of the influence of surface crevices on the tensile strength even for amorphous materials.

All the experiments described lead us to the conclusion that the practical weakness is principally due to sharp discontinuities mainly present on the surface and cannot be ascribed to small internal faults, "Lockerstellen" mosaic structure, or the like. In special cases only, there might exist an internal discontinuity of the same kind as a surface crevice.

Internal faults of a real crystal are however important for the mechanical behaviour as they increase the elastic limit and thus change the distribution of concentrated stresses responsible for the rupture at low temperatures. On the other hand, initial irregularities may lead by a plastic gliding to a sharp discontinuity on the surface, where the breakdown starts.

539.375

ON THE MECHANISM OF BRITTLE RUPTURE

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ABSTRACT. A considerable amount of experimental evidence is collected together to show that the weakness in tension of substances such as glass and quartz is due to irregularities on the surface. Thus it is well known that the strength decreases with increasing thickness; it is now shown that dissolving away a layer from the surface of a glass rod has the same effect as drawing it down in a gas flame. Again, the effect of the absorption of different vapours on the surface has been investigated. Other experiments show that irregularities of the kind postulated are distributed throughout the volume of the material, but that they only become harmful to the strength when they reach the surface.

The statistical distribution of strengths among a number of individual samples is in harmony with the theory, as also is the effect of altering the length of the sample.

The highest value found for the strength of rock-salt is 160 kg./mm² as against the normal value of 0.4 and the theoretical one of 200.

It has been shown that the surface has a deciding influence on the tensile strength both of single crystals and of amorphous bodies. The best way of studying the physical nature of this influence was an investigation of thin sheets and thin fibres, which was carried out by Jurkov and Alexandrov and gave valuable information on the appearance of cracks and discontinuities leading to breakdown.

Since the work of Kwinke it is well known that the tensile strength of thin wires increases as the thickness decreases. The dependence of the strength P on the diameter r of the wire can be represented by the formula

$$P = a + \frac{b}{r},$$

just as if the whole load were partly carried by the cross-section and partly by the perimeter. Kwinke assumed that the second effect was due to the surface tension of the solid wire. However, the experimental value of this effect came out about one thousandfold the real surface tension.

²²Griffith then assumed that a thin sheet of oriented molecules covers the surface of a glass fibre and has a very much higher strength than normal glass. This view seemed to be supported by experiments of Reinkober, who found an increase of elastic modulus for thinner glass fibres.

Jurkov was able to show that Reinkober's results were due to an experimental error. Measuring the stretching of a fibre, Reinkober neglected the displacement of the suspension point. The modulus of glass and quartz came out rigorously independent of the thickness, when this error was corrected.

The following experiments give a conclusive disproof of Griffith's hypothesis: a glass rod of about 1 mm^2 cross-section was etched in a solution of fluoric acid down to a diameter of 60μ . In spite of the removal of the thick surface layer which had been held responsible for the abnormal high strength, the thinner filament had a strength 3 to 5 times larger than the thick rod. The strength of filaments prepared by solution of the surface layer was just the same as that of filaments of the same thickness prepared in the usual way in a gas flame.

The influence of the surface has been best demonstrated by absorption of different vapours on the surface of glass and quartz filaments. Compared with a dry surface strained in a good vacuum, filaments decreased their strength by about fivefold in water vapour, about threefold in alcohol and twofold in benzol vapour. It was also shown that more than one molecular layer is necessary to produce the whole effect.

Dissolving a few microns of the surface layer in fluoric acid, Jurkov found a manifold increase in strength for any thickness of the filament. The dependence of the strength on thickness remained of the same nature both for normal and for etched glass and quartz filaments.

It was thus obvious that the usual weakness of glass and quartz was due to sharp irregularities on the surface of filaments. The next question was whether any such irregularities existed *inside* the glass rod. The tensile strengths of glass filaments have been measured during the process of solution. If faults of the same sharpness were distributed through the whole cross-section, then after a certain time some of them must appear on the surface. As the smoothing of such faults takes place gradually and slowly, while the elastic stresses appearing on a sharp end of a fault spread out with the velocity of sound, we should expect that this would lead to rupture just in the same way as without dissolving. In fact there was no difference between an ordinary filament loaded in air and a dissolved filament loaded in the fluoric acid solution. Even a filament made strong by etching in fluoric acid regained its initial weakness as soon as it was plunged into the same solution.

We conclude from these experiments that faults of the kind responsible for the rupture are distributed throughout the bulk of glass and quartz. They become dangerous however only on reaching the surface.

The mechanism of the growth of surface crevices was studied by Grebenshchikov who showed that the surface of glass is usually covered by a colloidal sheet which swells on absorption of water. In a crevice, the swelling of colloidal silica thrusts the walls asunder and produces a quite measurable stress which was directly observed by Grebenshchikov. In this way every surface crevice is already stretched to a high degree by the colloid; it takes a small additional load to let the crevice grow.

The point of view developed so far does not explain the existence of a definite value of mechanical strength for every material. We should expect the initial irregularities, which give rise to a surface crevice, to be of different sizes and shapes. According to the nature of the initial crevice, the stress necessary to cause it to spread would be different. Thus all strengths, up to the theoretical strength, should

be possible. The explanation is given by the large number and statistical distribution of faults inside a large body.

Just as in the case of Brownian molecular movement, the statistical character of heat motion becomes evident only for very small particles, and statistics of strength can directly be shown on small samples. The shorter and thinner the glass filaments, the larger the fluctuations in the value of strength. Among 100 samples of pyrex glass about 100μ thick, 1 had a strength of 12 kg./mm²; 4 of 15 kg./mm², 14 of 17 kg./mm², 20 of 20 kg./mm², 27 of 25 kg./mm², 18 of 27 kg./mm², 11 of 30 kg./mm², 4 of 35 kg./mm² and 1 of 43 kg./mm².

Fluctuations were large in glasses of complicated chemical composition and much smaller in pyrex or in quartz filaments. The number of samples of a given thickness plotted against the value of strength always gave something like a Gauss error curve, which has nothing to do with experimental errors.

The natural hypothesis which explains these observations easily, assumes a variety of faults inside the body. When they reach the surface they give a variety of discontinuities with differing influence on the strength. The most dangerous crevice only is responsible for the observed strength. It is of course natural to assume that the probability of a fault of given sharpness increases with decrease in the size of the fault; thus, there are few very dangerous faults. Loading a big rod with a large surface we expect a large probability of encountering such a fault; the observed strength is therefore always small and most probably of about the value given by the worst faults. The thinner the filament the smaller is the probability of a really dangerous crack on the surface. As the surface decreases, the most probable faults become smaller and smoother, and the discrepancy between the observed and the theoretical strength becomes less. But even among the thinnest filaments there are always found a few samples of much smaller strength. It is clear that the largest possible size of a crevice is limited by the size of the filament. Larger faults have already destroyed the sample before it can arrive at its final thickness. It appears that the fluctuation for the thinnest filament does not reach exactly the lowest limit of a large rod.

From this point of view the length of a filament ought to have the same influence as the thickness. The probability of a given strength is given by the whole surface. In fact the average strength for 100μ filaments about 5 cm. long was 42 kg./mm², while for 9 cm. it came down to about 32 kg./mm²; for 200μ short filaments we found 22 kg./mm² and, for long ones, less than 15 kg./mm².

The average strength of glass filaments for a given thickness is independent of temperature up to the temperature where glass becomes plastic (400–600° C.). From this point the strength decreases and at the same time fluctuations in the values of strength become smaller. The brittle rupture of glass changes into a plastic rupture.

If the explanation given above is correct, we may conclude that the highest values of strength found for the thinnest filaments or for an arrangement where surface crevices are avoided or made ineffective, must approach the theoretical value. It is, therefore, of interest to compare the highest measured value with the expected.

For rock-salt in hot water we have often found 10 kg./mm², in a few cases still more—30 and 160 kg./mm²; Piatty observed values of the same order or still higher, while the values of Smekal and his school are somewhat lower (5–6 kg./mm²). The theoretical value is about 200 kg./mm² and the normal one 0.4 kg./mm². It is quite probable that the rupture of rock-salt is a plastic one. For thick sheets of mica, the highest strength observed by Orowan was 320 kg./mm², while the usual value is 25 kg./mm². For thin sheets Walter found values up to 500 kg./mm². For thin quartz fibres, Jurkov found about 2,000 kg./mm² instead of 100 kg./mm²; for thin glass filaments 400 kg./mm² instead of 10 kg./mm².

These figures seem to show that the theoretical value of mechanical strength may be correct. The practical weakness is sufficiently explained by the Griffith crack theory. The statistical nature of the real strength is in good agreement with this theory.

539.375:548

THE RUPTURE OF PLASTIC CRYSTALS

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ABSTRACT. Sensitive processes start from nuclei (e.g. Griffith cracks for rupture or dust particles for condensation of a vapour). Their sensitivity is caused by two circumstances: (1) The intensity of the external influence (e.g. load or supersaturation as the case may be) necessary to start growth from the nuclei may depend considerably on their size (or quality). (2) The whole process may be initiated by a single nucleus or a few nuclei.—An important difficulty of the crack propagation theory hitherto has been the enormous crack lengths required by the Griffith formula for explaining the technical strength of plastic crystals. Besides the statical notch-effect considered by Griffith, there exists, however, another possibility for the development of cracks by means of plastic slip. By taking this into account, the necessity of assuming unduly large crack lengths can be avoided. Thus the crack propagation theory is to be regarded as satisfactory. On the other hand, proofs are given showing that no secondary or block structure explanation of the technical tensile strength is possible.

I

THE classical physics of crystals deals with properties which are remarkably insensitive to impurities and physical defects. Thus even if a crystal, embedded in a rock, has suffered considerable alterations by plastic flow of the rock masses, its refractive index and density remain so uninfluenced that very important methods of petrographical analysis can be based upon these properties.

It is easy to understand why these properties are so insensitive. They result from additive contributions of all lattice particles; now if the contribution of an anomalous or anomalously located particle is of the same order of magnitude as that of a normal one and if, besides, the number of anomalous particles is not too large, they cannot sensibly influence the property.

On the other hand, the additivity of a property is not sufficient to make it insensitive if the contributions of the anomalous particles are of a higher order of magnitude. Such a case is represented, e.g., by diffusion in a crystal. Here the particles are held fast in their places by potential barriers; in order to take part in diffusion they must first be set free. If this is effected by thermal agitation, then the number of particles made available for diffusion during a certain time is given

by the Boltzmann expression $e^{-\frac{E}{kT}}$, where E is the height of the potential barrier. This expression in general also determines the intensity of diffusion. For particles which are anomalously located (e.g. at an internal surface) the potential E is generally lowered, though it remains of the same order of magnitude. If, however,

the temperature is low enough, then the absolute value of the exponent in the Boltzmann expression is so large that a slight decrease of E can cause an increase $\left\{ \frac{E}{kT} \right\}$ of the expression itself—that is, of the intensity of diffusion also—by many powers of ten. So it can occur that in a certain temperature interval the overwhelming part of diffusion is performed by anomalous particles, the process being then sharply influenced by defects and impurities of the crystal.

The mere fact that some properties of this kind can be sensitive in one temperature interval and insensitive in another shows that this sort of sensitivity is not of the very essence of the phenomenon, but can be regarded as an unusually large contamination effect. In many cases, indeed, it is possible to separate the contribution of the defects and impurities and so to obtain, even in sensitive intervals, the value pertaining to the perfect crystal. A very important achievement in this respect has been made recently by Renninger⁵⁸*. Rock-salt has been regarded hitherto as a characteristic case of an X-ray mosaic structure; Renninger, however, has found that some artificially prepared specimens of it show no trace whatever of a mosaic structure but behave as perfect crystals according to the dynamical theory of Darwin and Ewald.

A particularly simple example of the enormous influence of trivial defects and of the possibility of separating them from the true value for the perfect crystal is presented by the vibration-damping capacity of mica†. Ordinarily, pieces of mica give, if struck, a sound similar to cardboard; thus the vibration damping must be very intense. If, however, by a special kind of very gentle cutting the crushing of the edges into lamellae is completely avoided, then the specimen clinks as clearly as a piece of hardened steel. The great vibration-damping capacity of ordinary pieces of mica is thus almost entirely produced by trivial injuries and not by an inherent system of faults such as would be represented by a secondary or block structure.

Properties of this kind which are of additive character, yet incidentally sensitive because of the great influence of anomalous particles, may be called, for shortness, *semi-sensitive* properties. To this group also belong electric conductivity of semiconductors, X-ray extinction and some photoelectric properties.

iii) In contrast to these, the sensitivity of a third group of even more sensitive properties is, from a theoretical standpoint, of the greatest interest. To this group belong tensile strength, shear strength (in other words, plasticity phenomena), dielectric strength and some properties of ferromagnetic materials. It is easy to see why strength properties are of an extreme sensitivity. The strength of a body is determined by the strength of the weakest part of it; thus a single minute scratch is sufficient to create a weak cross-section in a rod and to lower its tensile strength in extreme cases by tenfold or even more. Because of the decisive rôle of a few of the most critical faults we can appropriately speak of a *selective* character of strength properties, in discriminating them from the *additive* character of the insensitive and semi-sensitive properties.

* M. Renninger, *Naturwiss.* **22**, 334 (1934).

† E. Orowan, *Z. f. Phys.* **87**, 749 (1934).

Thus the following classification of the properties of solid matter, and especially of crystals, is obtained:

Property	Insensitive	Semi-sensitive	Sensitive
Character	Additive. Contribution of anomalous parts of the same order of magnitude as that of normal parts	Additive. Contribution of anomalous parts of a higher order of magnitude than that of normal parts	Selective
Examples	Specific gravity and heat, refractive index, X-ray interference pattern, elastic properties	Electric conductivity of non-metallic crystals, diffusion, X-ray extinction, vibration-damping	Tensile strength, plasticity, dielectric strength, magnetization curve of ferromagnetic bodies

As the sensitivity of the semi-sensitive group is of a rather trivial character, the following considerations may be confined to the third group only.

II

The source of most problems concerning strength properties is the well-known discrepancy between theoretically calculated strength and the actually observed value, which may be called "technical strength." If the law of force between the particles of a lattice is known, then for any given strain the corresponding stress can be calculated. For increasing strain, the stress will have a maximum value which is evidently the tensile strength of the lattice. Such a calculation was made in 1923 for rock-salt by F. Zwicky* who obtained a theoretical tensile strength of 20,000 kg./cm², which is about 1000 times as large as the actual technical strength of that crystal. In spite of this discrepancy the calculation cannot be incorrect; a second method which is quite different and perhaps less risky, indeed, leads to the same result. This method, suggested by Polanyi, makes use of the surface energy, which is defined as the work necessary to increase the surface of the body by a unit area in a reversible way. For a rough approximation the need of reversibility may be neglected and the surface energy applied for calculating the work which must be performed when by rupture a new surface of known size is created. If, moreover, the assumption is made that Hooke's law holds good until, at the moment of rupture, the stress suddenly drops to zero, then the mutual potential energy between two parts of the body can be calculated; at the moment when during the increase of strain the mutual energy per unit cross-section reaches twice the surface energy, rupture takes place. Hooke's law gives now the simultaneous stress which presents a rough approximation to the theoretical tensile strength. The result for rock-salt is very much the same as that of the direct calculations from lattice theory.

The method of surface energy is applicable in all cases if only an approximate value of the surface energy (whose square root enters into the result) is obtainable.

* F. Zwicky, *Phys. Z.* 24, 131 (1923).

It is very important that in this way we can calculate the theoretical strength of amorphous bodies and that *here the same discrepancy exists as in the case of crystals*. Even from this fact alone it is rendered most probable that the discrepancy cannot arise from features peculiar to crystals, such as a secondary or block structure.

We may notice that tensile stress has in the case of amorphous bodies the same degree of sensitivity as in the case of crystals. At this point it may also be emphasized that sensitive phenomena are not confined to the crystalline state; they can also appear in amorphous bodies and even in liquids and gases. Thus dielectric strength can be regarded as a sensitive property of gases.

A discrepancy which is quite analogous to that between theoretical and technical tensile strength exists also between theoretical and technical dielectric strength and shear strength of crystals.

III

Till now, two entirely different possibilities for explaining the discrepancy between theoretical and technical tensile strength have been suggested, viz. the Griffith theory of rupture and the various secondary structure and block structure hypotheses.

According to Griffith*, the discrepancy is a consequence of the fact that rupture does not take place simultaneously over the whole cross-section of a body, but that it starts from a crack or other inhomogeneity and extends gradually, before the average stress even approaches the theoretical strength. If an absolutely simultaneous rupture along the whole cross-section could be attained, the body would show the theoretical tensile strength. As to the cause of premature rupture, Griffith assumes that the inhomogeneity of stress distribution in the neighbourhood of flaws produces an increase of the average stress in the ratio of the theoretical strength to the technical strength. Thus the theoretical tensile strength is reached at the edge of a crack at the moment when the average stress has the value appropriate to the technical strength. We may assume that the Griffith conception of rupture as a crack-propagation process is to be regarded as proved true. The only addition that must be made in the case of plastic crystals is that here, besides the notch-effect considered by Griffith, another possibility for the premature propagation of cracks must be assumed, namely, a propagation by means of plastic slip. For rock-salt, for example, the depth of cracks required by the Griffith formula for explaining the discrepancy between theoretical and technical strength would be about half a millimetre; for zinc or tin crystals even more. This difficulty of the Griffith theory has played an important rôle in the formation of the various secondary and block structure hypotheses; its solution, however, is very simple. For plastic crystals there exists, besides the statical notch-effect as calculated by Griffith, another possibility for the extension of cracks. This may be explained in the case of rock-salt.

Let AB be a surface crack in a cube plane perpendicular to the direction of load

* A. Griffith, *Phil. Trans. Roy. Soc. A*, 221, 180 (1921); *II. Internat. Congr. for Appl. Mech.* Delft, 1924, p. 61.

(Figure 1). If at the point C in the plane of slip CD a slip starts, then the parts already slipped pull the other parts of the plane after them until the slipped part is extended to the point P which is in the continuation of the crack. Now the material remaining between P and the edge A of the crack must sustain a stress which is sufficient to transfer the process of slipping to the part PD below the crack; otherwise it will tear along PA and the crack will be deepened by the distance PA . Since we know empirically that a process of slipping is never confined to a single plane but spreads out continuously to the neighbouring planes, in many cases a further deepening of the crack will occur which leads either directly to rupture by a continuation of the same process, or indirectly by a Griffith mechanism, if meanwhile the critical crack depth has been reached.

Now the question arises whether by this mechanism the necessity of assuming very deep cracks can be avoided. The tensile strength of the minute part between P and A is evidently very near to the theoretical strength; on the other hand, for obtaining a most unfavourable case, the force necessary to move the triangular piece DBP must be calculated from the technical shear strength by multiplying by the length of the hypotenuse DP . By omitting sines and cosines which cannot alter the orders of magnitude, we obtain as a condition for rupture along the line PA

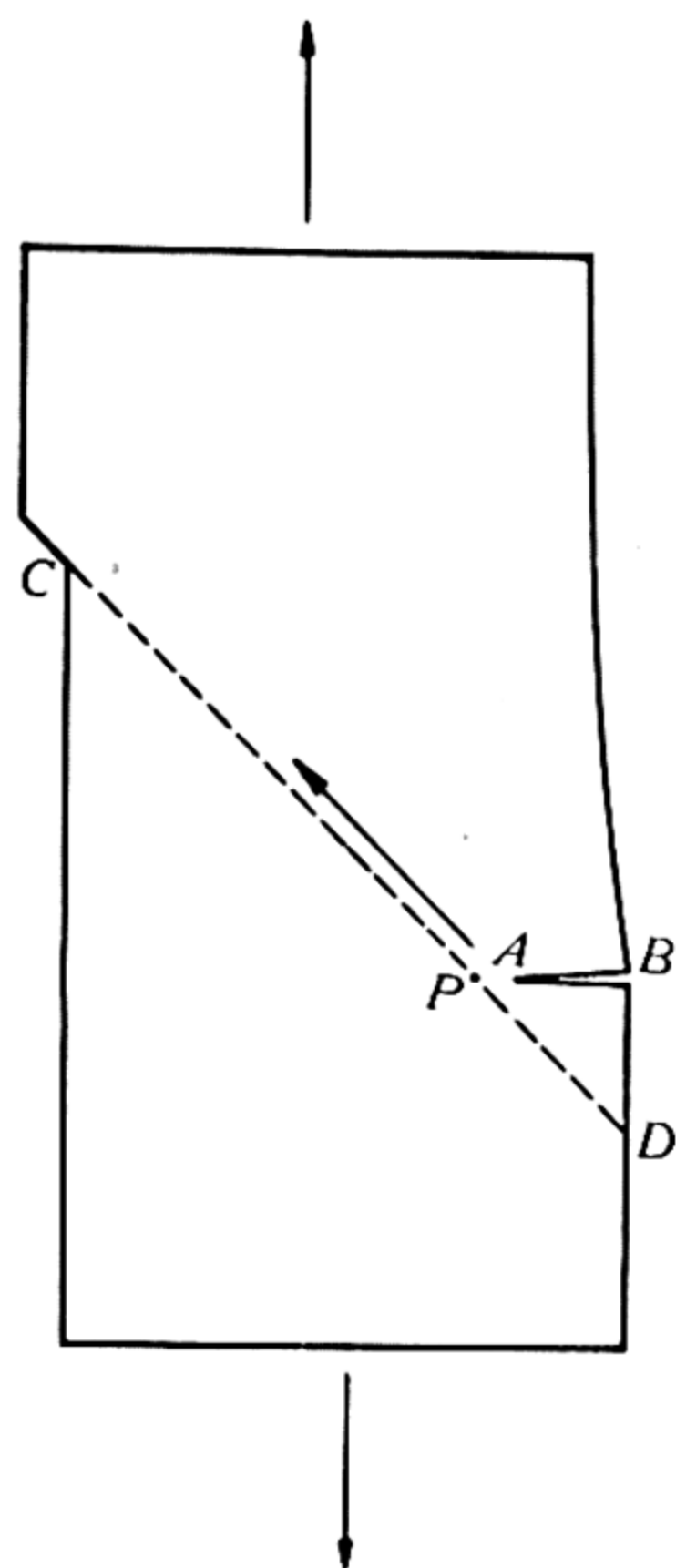


Figure 1

$$PA \cdot z_0 = DP \cdot s,$$

where z_0 denotes the theoretical tensile strength of the cube plane and s the technical shear strength of the (110)-plane. We take PA to be several times the lattice distance ($a = 2.86 \text{ \AA}$. for rock-salt); since the ratio z_0/s is about 1000 we obtain for the minimum crack depth DP an order of magnitude of 1 micron. This is quite a satisfactory value.

We may mention that the formation of visible cracks, evidently by a slipping mechanism, has been observed on several occasions in zinc and rock-salt crystals. So the actual occurrence of this process stands beyond doubt.

The crack propagation theory of rupture accounts not only for the discrepancy between theoretical and technical strength but also for other important features of tensile strength. Moreover it does not encounter any essential difficulties.

IV

A second way, quite different from the crack propagation theory, for explaining the discrepancy between theoretical and technical strength, is presented by the various *secondary* and *block structure hypotheses*. According to these, a crystal is built of very small blocks whose lattice is ideal, showing the theoretical strength as

calculated by means of lattice theory or of a known surface energy. These blocks are, however, separated from one another by layers of disordered particles so that the cohesion between two neighbouring blocks is much lower than its internal strength; it is assumed to be equal to the technical strength of the crystal.

As to the cause of secondary structure, two possibilities exist. The *secondary structure hypotheses* in a strict sense, as pointed out by Zwicky*†, suppose that the formation of a secondary structure is accompanied by a decrease of the free energy of the crystal; thus a crystal with a secondary structure represents an equilibrium configuration which always results if the crystal remains uninfluenced during a sufficient time. The *block structure hypothesis* of Smekal‡, on the other hand, regards this structure as an inevitable imperfection of the crystal, originating perhaps in the finite speed of its growth. According to Smekal, the equilibrium configuration is given by the ideal lattice; a real crystal would lose its secondary structure if left uninfluenced for a sufficiently long time; this case, however, could not be realized, as otherwise the crystal would obtain its theoretical strength in contradiction to experience.

Zwicky has made two attempts to derive theoretically the existence of a secondary structure. He considered two entirely different arbitrary alterations in the lattice of crystals of the rock-salt type and he tried to show that these alterations would be accompanied by a decrease of the energy of the crystals. If this holds good, then a spontaneous formation of a secondary structure can be expected.

The starting point of Zwicky's first secondary structure hypothesis* is the fact that a (100)-lattice plane of a crystal of the rock-salt type contracts if set free. According to the calculations of Lennard-Jones and Dent§ the linear contraction amounts in the case of rock-salt to 6 per cent. Though a spontaneous contraction is of course subject to the condition that the plane shall be isolated, Zwicky made the assumption that a contraction of the same amount could also take place spontaneously in the interior of the crystal. He postulated, then, that a minimum of energy is reached when three orthogonal sets of parallel planes are contracted; as to the distance of two consecutive parallel planes, he assumed it to be much greater than the distance of two lattice planes. So the sets of contracted planes would form a secondary structure in the crystal.

For verifying the assumption of the spontaneous contraction of internal lattice planes, Zwicky tried to prove that a gain of energy results from contracting an internal (100)-plane in the ratio calculated by Lennard-Jones and Dent for isolated planes. By calculating the different kinds of energy changes connected with the contraction, he was led in his first detailed paper to the following energy balance:

* F. Zwicky, *Proc. Nat. Acad. Amer.* 15, 253, 816 (1929); *Helvet. Phys. Acta*, 3, 269, 466 (1930); 4, 49 (1931); *Proc. Nat. Acad. Amer.* 17, 524 (1931).

† F. Zwicky, *Proc. Nat. Acad. Amer.* 17, 524 (1931); *Phys. Rev.* 38, 1772 (1931); 40, 63 (1932).

‡ A. Smekal, *Wien. Anz.* p. 191 (1925); *Ann. d. Phys.* 83, 1202 (1927).

§ J. E. Lennard-Jones and B. M. Dent, *Proc. R. S. A*, 121, 247 (1928).

Gains of energy:	erg./cm ²
by the contraction itself	82
by the polarization of ions of the contracted plane and of two neighbouring planes	457
by an accessory change of energy	28
	<hr/>
	Sum 567
Loss of energy:	
by increase of the mutual energy between the contracted plane and neighbouring parts of the crystal	500
	<hr/>
Total gain	67

According to this balance, a small gain of energy would be obtained; it is, however, disquieting that the initial gain by the contraction itself is quite unimportant as compared with the other changes of energy and that the total gain represents only a small difference between the two sides of the balance. Afterwards it was found by Prof. Pauling that the calculation of the energy loss was erroneous; the correct value, calculated then by Zwicky himself, amounts to 1140 erg./cm², instead of 500. By this the existence of a secondary structure in rock-salt and also the general existence of a secondary structure of this kind has been proved impossible. Zwicky, however, laid much stress upon the fact that in two cases, viz. PbTe and PbS, even after correction, a gain of energy* results. Yet later* it was found possible to show that the balance contains another miscalculation of a still greater importance. For determining the polarization energy, the electric field strength at the position of every ion must be known. Along the contracted plane or the neighbouring planes, the field strength is represented by products of trigonometrical functions of the two coordinates. Referring to the difficulty of an exact calculation, Zwicky contented himself with calculating the field strength at one particular place and determined the polarization energy by means of this value, declaring that this approximation could not alter its order of magnitude. Now such an approximation is of no use since the total energy change by contraction is given as the difference of two almost equal quantities. Moreover, the field strength assumed by Zwicky was unfortunately just its maximum value; by carrying out the calculation of the polarization energy exactly*, a value results which is one-third only of the polarization energy obtained by Zwicky (152 erg./cm² instead of 457 erg./cm²). As the polarization energy represents the decisive part of the total energy gain, this correction converts the balance for every crystal into a large loss. In other words, the calculation of Zwicky shows, if corrected, that *a secondary structure of this sort is impossible*.

An entirely different kind of secondary structure, also suggested by Zwicky†, arises from a generalization of a feature of ferromagnetism. Ferromagnetic bodies possess a spontaneous magnetization, even in the absence of an external field. If the body is, as a whole, unmagnetized, the direction of the spontaneous magnetization must be assumed to vary from place to place, in order to avoid a resulting magnetic moment. Magnetization gives rise to magnetostriction which must likewise vary in different parts of the body, if no saturation has yet been reached. Thus

* E. Orowan, *Z. f. Phys.* **79**, 573 (1932); **89**, 774 (1934); *Helvet. Phys. Acta*, **7**, 285 (1934).

† F. Zwicky, *Proc. Nat. Acad. Amer.* **17**, 524 (1931); *Phys. Rev.* **38**, 1772 (1931); **40**, 63 (1932).

internal stresses are created, causing deviations from the ideal lattice. A phenomenon which represents an electric analogue to ferromagnetism has been observed by Joffé and his collaborators in crystals of the rochelle salt type.

Now Zwicky has postulated that a spontaneous polarization, either magnetic or electric, is quite a general property of crystals; the accompanying internal electro- or magnetostriction represents a secondary structure which he makes responsible for the sensitivity of strength properties and for the discrepancy between theoretical and technical strength. As an argument in favour of a general occurrence of spontaneous polarization, Zwicky makes a calculation from which he finds that certain crystals of the rock-salt type must show such a phenomenon.

It is perhaps unnecessary to devote a more detailed criticism to this hypothesis as its insufficiency is evident. Firstly, a spontaneous polarization is, as a matter of fact, quite a particular phenomenon whose non-existence can be granted for the overwhelming majority of crystals, especially also in the cases to which Zwicky's calculations refer. Secondly, according to that hypothesis, strength properties should show a complete change at the Curie point or near saturation. So it need only be mentioned as an explanation of the contradiction between experience and the calculations of Zwicky, that the cardinal point in these is the value assumed for the *second derivative* of the repelling force, for which Zwicky uses the simple exponential expression with a repulsion constant obtained as usual from measurements of compressibility. Now Slater* has shown by measuring the pressure coefficient of compressibility that this expression represents no approximation whatever for the second derivative of the repelling force; so the calculations of Zwicky are illusory.

Although the attempts of Zwicky for deriving a secondary structure in crystals have failed, it could perhaps be imagined that a hitherto unknown third kind of secondary structure exists, producing the principal features of technical strength. Such a secondary structure could be either of the Zwicky type, corresponding to a minimum of free energy, or of the Smekal type (a block structure, caused by inevitable irregularities or by the finite speed of the crystal growth). Now it is of the greatest importance for the theory of sensitive properties that it should be possible, by using some well-known empirical facts, to show in an exact manner that an explanation of the phenomena of technical strength by means of any secondary or block structure hypothesis is impossible. This statement can be proved in the following way†.

If a secondary structure were responsible for the discrepancy between theoretical and technical strength, then approximately the same discrepancy would exist between the theoretically calculated and actually observed values of surface energy. The sphere of action of the molecular forces between two parts of a crystal remains, indeed, practically unaltered on assuming a secondary structure; thus the work necessary for separating two parts of the crystal, in other words, its surface energy, must diminish in about the same ratio as the force, i.e. the tensile strength.

* J. C. Slater, *Phys. Rev.* **23**, 488 (1924).

† E. Orowan, *Z. f. Phys.* **82**, 239 (1933).

For example, the surface energy of the cube plane of rock-salt, calculated by means of the lattice theory, is about 90 erg./cm². Since the ratio between theoretical and technical tensile strength is 1000, an observed surface energy of approximately 0.1 erg./cm² is to be expected if the secondary structure hypothesis holds good. Now although an exact measurement of the surface energy of rock-salt has not yet been possible, many approximate measurements have without exception given values of the calculated order of magnitude, in general even somewhat more. A discrepancy amounting to even one decimal place is surely impossible.

Another striking example is given by mica. This crystal possesses an extraordinarily perfect cleavage plane; its tensile strength in a direction perpendicular to this plane must be very small and even the mere preparing of a rod with an axis in this direction would hardly be possible because of the danger of premature breaking. Thus a very low value for the surface energy of the cleavage plane should be expected if the perfect cleavage is caused by a block or secondary structure. Contrary to this, very reliable measurements of Obreimoff* show that actually the observed surface energy of this plane is about 5000 erg./cm² which is perhaps the highest known surface energy.

These examples are sufficient to show definitely the failure of all secondary and block structure hypotheses. Yet there exists still another argument leading to the same conclusion. If the technical tensile strength of a crystal had to be attributed to a secondary structure, then it could be increased only by altering this structure. Now in the case of mica it is possible to obtain an increase of tensile strength of tenfold by a mere surface treatment. The bounding surfaces of a mica lamella are of two kinds: firstly, two principal cleavage planes of the utmost perfection; secondly, side surfaces forming the edge, which are in general not crystallographic planes and which can usually only be obtained by cutting or grinding. These edge surfaces contain numerous cracks easily observable at a moderate magnification. Thus the assumption that these cracks influence the tensile strength of the lamella according to the Griffith theory is plausible; in other words, that the normal technical strength of mica bands is given by the average stress necessary for the edge cracks to start propagating themselves across the lamella.

That this assumption holds good can be shown by a simple artifice†. If the clamps used for applying the load are narrower than the mica band, then the side borders, being beyond the clamps, bend up at loading and they become nearly stressless so that no propagation of edge cracks can start. In this case the tensile strength of the mica lamella is increased tenfold, a maximum strength of 32,000 kg./cm² having been observed instead of the usual value of about 3000 kg./cm². Now if the strength of mica in a direction parallel to the principal cleavage plane was determined by the cohesion of neighbouring blocks according to the various secondary structure hypotheses, then it would be capable of no further enhancement, the secondary structure of the individual crystal being given once for all. So this experiment proves directly that the technical strength of mica crystals is determined

* J. W. Obreimoff, *Proc. R. S. A.*, 127, 290 (1930).

† E. Orowan, *Z. f. Phys.* 82, 235 (1933).

by a system of trivial cracks and that an explanation by means of a secondary or block structure hypothesis is impossible.

A third argument which is less direct but perhaps ^{N.B.} more impressive is offered by the fact already mentioned that there is no difference between crystalline and amorphous bodies so far as the discrepancy between theoretical and technical tensile strength is concerned. Since a secondary structure is possible only in crystals (if singular cases such as opal are excepted) the block structure hypothesis would attribute a uniform phenomenon to different causes.

By these arguments the impossibility of any secondary or block structure hypothesis is definitely proved. We see that the alternative, whether a hypothetical secondary structure can play an essential rôle in the theory of strength properties or not, is at the present state of things no matter of personal opinion, since the arguments against the secondary structure hypothesis are absolutely decisive. So the principal problem of tensile strength can be regarded as settled: all general features of it are produced by the fact that, according to crack propagation theory, rupture does not take place simultaneously in the entire cross-section but propagates itself gradually, starting from a singular point.

We may yet remark that amongst the defenders of secondary structure hypotheses it has become usual to support their view by enumerating as many empirically known cases of superstructure as possible. It is, however, clear that the very existence of superstructures as, e.g., the X-ray mosaic structure or the Bitter sedimentation stripes on ferromagnetic metals have nothing to do with the question whether a secondary structure plays an essential rôle in originating characteristic features of sensitive properties or not. As a matter of fact, no important case is known where even the individual strength properties of a particular crystal could be brought into relation with a particular superstructure observed in it. For example, the mechanical properties of steel remain practically unaltered on reaching the Curie point, when all superstructures of ferromagnetic origin would vanish. The X-ray mosaic structure can even be regarded as an approach to a polycrystal and thus must cause an increase of tensile strength, since the passage from one mosaic element to another represents a difficulty in the development of a crack.

V

Till now, we have almost exclusively considered examples concerning the tensile strength. Yet the recent progress of our knowledge on crystal plasticity enables us to derive from it ideas as detailed as those derived from the phenomena of tensile strength; these fit excellently into the picture we have made of a sensitive property in general*†.

We must omit to deal here with dielectric strength which is, however, so typically connected with a lability of a similar kind to the propagation of a crack, that no secondary structure hypothesis has ever made an attempt to deal with it in a detailed manner.

* G. I. Taylor, *Proc. R. S. A.*, **145**, 362, 388, 405 (1934).

† E. Orowan, *Z. f. Phys.* **89**, 605, 614, 634 (1934).

Attention may, however, be called to some sensitive phenomena in ferromagnetic crystals or polycrystals. Recent researches on the origin of technical permeability of ferromagnetic bodies led to the very interesting result that Barkhausen jumps do not take place simultaneously in a certain region of the body but propagate themselves with a relatively low speed*. As, indeed, R. Becker† has shown theoretically, they cannot result from a continuous turning of the direction of spontaneous magnetization in the direction of the external field, since such a process needs considerably stronger fields than those actually producing Barkhausen jumps. This phenomenon consists, on the contrary, of a gradual displacement of the partition-walls between Weiss regions, in such a manner that a region whose magnetization has nearly the direction of the external field extends itself. According to experiments of Sixtus and Tonks, a stronger external field is needed to start a Barkhausen jump than to continue it; this means that at starting we must overcome a sort of resistance. Considerations on the nature of this resistance have been put forward by R. Becker, Bloch, and Langmuir; it is very probably caused by the smallness of the initial Weiss region, in the same way as extreme smallness of a drop of water checks further condensation on it if the supersaturation is not large. The situation is thus quite similar to the Griffith theory: in the latter the load necessary for continuing the process of rupture decreases rapidly as the area already separated increases; the initial crack forms a *nucleus* for rupture whose size determines the strength.

These considerations lead us to a general characteristic of sensitive phenomena. In all such cases of sensitive phenomena, we have a process which can be regarded as *autocatalytic*; that is, its further development is facilitated if only it has started at a place which we call a *nucleus*. The creation of a nucleus needs a local accumulation of energy either from a material anomaly or from a thermal fluctuation. The amount of external influence (e.g. load) necessary for growth of a nucleus depends in a high degree on the amount of accumulated energy, and on the size and the nature of the nucleus; this great dependence, together with the possibility of spreading out from a single nucleus to a great part of the body, is the cause of the sensitivity.

Thus in the case of the rupture of a rigid body the nucleus consists of a crack which facilitates the process by its notch-effect. The load necessary for propagating the crack is, according to the Griffith formula, inversely proportional to the square root of the crack depth; so the rupture runs on, once initiated, with a high acceleration.

In the case of crystal plasticity, the nucleus is given by a local slip§, originated both by a material inhomogeneity and an additional thermal fluctuation. The local slip facilitates further slipping by producing a zone of dislocations‡ around itself. Very probably the nuclei of Barkhausen jumps, causing the irreversible part of the ferromagnetic permeability, due to displacements of Weiss walls, are produced also by the compound influence of material inhomogeneities and thermal fluctuations.

* Sixtus and Tonks, *Phys. Rev.* 37, 930 (1931).

† R. Becker, *Phys. Z.* 33, 905 (1932).

‡ G. I. Taylor, *Proc. R. S. A.* 145, 362, 388, 405 (1934).

§ E. Orowan, *Z. f. Phys.* 89, 605, 614, 634 (1934).

The electric breakdown of a crystal takes place if a single ion acquires a sufficient amount of energy during its movement in the electric field. As the technical dielectric strength is comparatively low, the ion must, for acquiring the necessary energy, have a long path available which is only possible if the crystal contains an imperfection either innate or due to thermal fluctuations. The energy represented by this imperfection can be regarded as the work necessary for creating a nucleus.

We now see that boiling, freezing, condensation, and more generally all changes of phase are to be ranged in a most natural manner amongst sensitive phenomena of a selective character. It will suffice to point to the phenomena of superheating, undercooling and supersaturation; with respect to sensitivity there is no difference between these phenomena and tensile strength, plasticity or irreversible permeability. Their common feature is the rôle of nuclei and the accelerated spreading out of the phenomenon from these. As far as the principle is concerned it is irrelevant whether the nuclei are Griffith cracks, local slips, thermal fluctuations of stress or, on the other hand, dust particles or gaseous, solid, or liquid nuclei produced by thermal fluctuation. We may, however, notice that theoretical strength and condensation-point for example, as defined thermodynamically, are not analogous but opposite quantities: a condensation pressure obtained in a reversible way presumes the presence of very active nuclei; thus it is to be regarded as similar to the highly reproducible tensile strength of mica lamellae, obtained by grinding the edges and providing them in this way with a large supply of cracks*. The quantity corresponding to theoretical strength in the case of condensation at a constant temperature would rather be the maximum of the van der Waals p - v curve which is in practical cases cut away by the Maxwell horizontal.

In summarizing the results, we can say that the foundations of the theory of strength properties are to be regarded as clear. The main features of strength phenomena arise from the fact that every breakdown, either mechanical or electrical, starts from minute nuclei which have a decisive influence on strength. On the other hand, an explanation of strength properties by means of secondary structure hypotheses is not only unnecessary but is also impossible.

* E. Orowan, *Z. f. Phys.* 82, 247-251 (1933).

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THE STRUCTURE-SENSITIVE PROPERTIES OF SALT CRYSTALS

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ABSTRACT. A structure-sensitive property is one which has different values in different specimens of the same crystal, the actual states of a crystal being of a characteristic metastability. A crystal with structure-sensitive properties must clearly require more variables for its description than the ideal stable crystal, and the simplest model to take is that of an ideal lattice crystal, modified by the presence of gaps of some variability in number and kind.

The observed metastability of the actual crystal for small changes of temperature shows that it really preserves the state in which crystallization occurred.

In the formation of crystals, growth in general takes place tangential to certain definite planes, the molecular character of the growth giving rise to gaps and to local variations in orientation, whilst the presence of impurities leads to the incorporation of foreign atoms. These are all classified as primary flaws, and they are statistically distributed along the principal planes of growth. Secondary flaws are those which result from the alteration of the primary flaws, or from the formation of new flaws in the solid state by mechanical or thermal treatment of crystals. They may reach much greater size than the primary ones.

The relations, statistical and other, to be expected theoretically between flaws and structure-sensitive properties dependent on them, are briefly summarized.

The second section of the paper deals with experimental results obtained on rock-salt, which was chosen for investigation after exhaustive consideration.

It is first shown that the photochemical coloration of rock-salt is a structure-sensitive property, and that by its aid the primary and secondary flaws in rock-salt can be marked.

As an example of general structure-sensitive properties, the strength is then discussed. The experimental determination of the pure macroscopic cohesion and of the elastic limit of rock-salt crystals are briefly indicated. When the connexion between cohesion, elastic limit and crystal flaws is examined, it is found that under mechanical stretching, the first permanent changes occur by local stress concentrations at the flaws, the maximal elastic stresses measured optically being of the order of the ideal lattice strength.

I. GENERAL THEORETICAL BASIS

§ 1. THE PHYSICS AND STRUCTURE-SENSITIVE PROPERTIES OF CRYSTALS

(1.1) *General statement of the problem*

EXPERIMENT gives sharply reproducible results for a large number of crystal properties, which can be satisfactorily explained on the basis of the ideal lattice theory of crystal structure, by means of the atomic-physical properties of the

crystal particles. Other crystal properties are characterized by the fact that they possess different values in different specimens of a crystal, and therefore are *not* describable in terms of the ideal lattice theory, which only permits of *definite single values for crystal properties*. I have contrasted these two groups of crystal properties as *structure-sensitive and structure-insensitive properties*, and have propounded as a task for the more recent crystal physics that it should explain *the simultaneous existence of these two contradictory types of properties in the same crystal**. Experimental results show that *cohesion, plasticity, and self-diffusion at low temperatures* are "general" structure-sensitive crystal properties of all materials, so that in each of these cases a *fundamental problem of crystal structure* is encountered. Other structure-sensitive properties, such as the photochemical properties of salt crystals or the magnetization curves of ferromagnetic materials, are confined to special groups of materials and must therefore in all cases be associated with special properties of the material.

(1.2) *The problem of stability and structure-sensitive properties*

The existence of general structure-sensitive properties indicates that a greater number of variables is necessary for the specification of the state of the crystal than that allowed by the ideal lattice theory or than that demanded by the specification of the structure-insensitive properties. The new quantities introduced must obviously permit only slight deviations from the ideal lattice, which in the general case will have different values from crystal to crystal. The individual, different states cannot therefore possess exactly the same stability. There are then two possibilities:

(a) The absolutely stable condition is the ideal lattice.

(b) The absolutely stable condition is a fundamental state differing in a definite manner from the ideal lattice.

In *both* cases however it is necessary that:

(c) The actual states of the crystal should in general differ both from each other and from the absolutely stable condition; also, on account of the slow rate at which equalization proceeds in the solid state, they should be only temporarily stable but secularly unstable.

(1.3) *The stability of crystal lattices*

The *absolute* stability of either a finite or an infinite crystal lattice cannot as yet be investigated or demonstrated theoretically. *Electrostatic* systems are of course of a fundamentally unstable nature to which all the criteria of stability so far investigated are inapplicable. Atomic physics and quantum mechanics have shown that the stability properties of a system of atoms are determined by *quantum-mechanical laws*. The full application of these to the crystal lattice is not as yet possible in any

* A. Smekal, *Proc. Inter. Cong. Phys., Como, 1927*, 1, 181 (Bologna, 1928); *Z. f. Phys.* 55, 289 (1929) and especially "Structure-Sensitive Properties of Crystals" in *Handbuch der Physik*, 2nd ed., 24, (2), chap. 5 (Berlin, 1933) (referred to below as "Structure-Sensitive Properties").

single case. For this, the whole crystal would have to be regarded as built up of atomic nuclei and electrons, full account taken of the spin and exchange coupling, as well as of the electrical, and the ground state of such a giant molecule determined. It is not at present possible to say whether this ground state corresponds to an ideal lattice or deviates slightly from it. Still less is it possible on these grounds to make any assertions as to the nature of the metastable excited states, which are concerned in the case of the structure-sensitive properties.

(1.4) *The point of view of the ideal lattice theory*

The ideal lattice theory assumes the absolute stability of both the finite and the infinite ideal lattice, although this stability cannot be proved. In addition, we can, with Born and Goldschmidt, establish the *relative* stability of the various *simple* lattices, the quantities, sizes and polarization properties of the atoms playing the main determining part. The only variable factor directly reconcilable with the ideal lattice theory, is the *area of the surface* of a finite lattice. Surface components and (internal) lattice components of the crystal possess some fundamentally different properties. Crystals of equal size but with different surfaces must show differences in their properties due to this difference. Since the trivial differences between the outer surfaces of macroscopic crystals are not of importance, there must be *differences attributable to internal surfaces* to account for the structure-sensitive properties. I have accordingly taken as *the simplest model of a crystal with structure-sensitive properties, a crystal built up according to the ideal lattice theory, but containing gaps**, the secular instability of which crystal as compared with the *ideal crystal* with no gaps needs no further demonstration. In any case there can be no theoretical inconsistency in the ideal lattice theory advancing along these lines towards a basic solution of the general problem (1.1).

(1.5) *The point of view of the instability theory of the ideal crystal*

The hypothetical denial of the absolute stability of the ideal lattice for all crystallizing materials leaves in doubt what are the actual crystal states of absolute stability. A further hypothesis is necessary to fix this state; with regard to crystal symmetry, a reference to the crystallographically defined elements of the general structure-sensitive properties seems to be involved, of which cleavage-, slip-, and twinning-planes as well as the principal direction of self-diffusion in the crystal structure might be selected since they are connected with certain stability properties of the structure. No reason is yet known for the preference for a definite plane or direction from among those enumerated. So far only two general statements of a *negative* character appear to be *demonstrable*: (a) In permanent lattice cells any regular deviation from the ideal lattice reduces the symmetry of the crystal. (b) If in the fundamental ideal lattice, definite planes forming a super-lattice are supposed to be physically changed, it is in general impossible to divide up the original lattice by these planes into congruent blocks if in the super-lattice all the

* A. Smekal, *Phys. Z.* 26, 707 (1925); 27, 837 (1926), also footnote, p. 94.

planes crystallographically equivalent to one of its planes, behave in an equivalent manner*. In the case of the secularly unstable states, which according to (1.2) are necessary to explain the structure-sensitive properties of a crystal, a similar reference to external and particularly to internal surfaces in the finite crystal lattice would be essential, as already mentioned under (1.4) in connexion with the ideal lattice theory, so that here also the crystal with gaps appears to be the simplest model.

(1.6) Zwicky's "secondary structure"

Zwicky postulates the fundamental instability of the ideal lattice in connexion with (1.1), and maintains that the absolutely stable crystal state is an ideal "primary lattice" with a "secondary lattice" of the super-lattice type referred to above†. More detailed description was not given by Zwicky of the nature of the empirical crystal states deviating from this assumption, so that his original views could yield *no* information as to the structure-sensitivity of crystal properties. As to how far his assertions regarding the absolutely stable state may be correct, it is only possible from them to deduce consequences which cannot be confirmed on any single material, on account of the absolute purity and perfection of the structure assumed. A stability *proof* of the fundamental necessity for a "secondary structure" is, as stated in (1.3), just as impossible as is that for the ideal lattice, a fact which Zwicky now admits‡. This being so, any possibility of deducing the secondary lattice corresponding to a given ideal lattice, as e.g. Zwicky has deduced that the secondary structure of the rock-salt lattice consists of the cube faces, becomes impossible. Hitherto Zwicky has not accepted this conclusion and believes that it can be supported by considerations of the electrostatic energy difference between lattices with and without this secondary structure. As stated in (1.3), however, electrostatic energy conditions alone cannot decide problems of stability; moreover we hold with Born and Orowan that the increase of electrostatic energy on the addition of a "secondary structure" claimed by Zwicky rests on faulty analysis§, and does not occur. There is thus at the present moment no certainty as to the instability of the ideal lattice. Other similar computations by Zwicky and Evjen deal with "secondary structures" which are only possible in certain lattices, i.e. selected groups of materials; we refrain from discussing these, as they are of no importance for the problem of the *general* structure-sensitive properties. The only theoretically certain "secondary structure" concerns the distribution of spin in the lattices of ferromagnetic crystals and according to Heisenberg is not of a regular lattice-geometrical nature; it is of considerable importance in the understanding of the special ferromagnetic structure-sensitive properties, but of no fundamental importance in connexion with the general structure-sensitive properties (strength properties) of the ferromagnetic materials.

* Important examples of theorem (b) are provided by all the regular or pseudo-regular crystals (diamond, rock-salt, aluminium, bismuth, etc.) if the super-lattice is regarded as consisting of the observed octahedral planes established here to be planes of cleavage or slip.

† F. Zwicky, *Proc. Nat. Acad. Amer.* 15, 816 (1929), and later papers.

‡ F. Zwicky, *Helv. Phys. Acta*, 6, 210 (1933), p. 213; A. Smekal, *Phys. Rev.* 44, 308 (1933).

§ M. Born and M. Goeppert-Mayer, *Handbuch der Physik*, 2nd ed., 24 (2), chap. 4 (1933); E. Orowan, *Z. f. Phys.* 79, 573 (1932); *Helv. Phys. Acta*, 7, 285 (1934); *Z. f. Phys.* 89, 774 (1934).

§ 2. THE STRUCTURE AND GROWTH OF CRYSTALS

(2.1) *Permanence of actual crystal states*

The existence of structure-sensitive crystal properties, as in (1.2) (c), implies the existence of individual crystal states, the differences and temporary stability of which are rendered possible by the slow rate at which equalization proceeds in the solid state. It follows from this permanence of the actual crystal states that the states occurring at the conclusion of crystal growth suffer little if any appreciable change in the absence of alterations in external conditions. The most obvious way therefore of accounting for the variety of actual states is to attribute them to the behaviour during growth. Additional more or less easily demonstrable changes in the crystal state can be produced, principally by thermal or mechanical effects, the nature of which changes will then depend on the prior history in the solid state.

(2.2) *Laws of crystal growth*

The laws governing infinitely slow crystal growth of a chemically pure material from a *single centre* have been elucidated by Volmer and Brandes, Kossel and Stranski; the ideal lattice is in this case built up by tangential growth along definite lattice planes of slowest growth, these planes having been calculated by Stranski for several types of lattice. For finite rates of growth the general tangential growth still takes place along these planes; the molecular character of the growth, however, expresses itself in deviations, which are such as to give rise either to the *presence of gaps* in the growing crystal or of *variations in orientation**, and which may be considerably assisted, especially by high-temperature crystallization†. The presence of impurities, which can practically never be excluded, leads to the *incorporation of foreign atoms*, in the form, depending on their nature, either of a solid solution or of inclusions (gaps) ‡—in the case of the very small amount of impurities present in the purest materials (10^{-4} to 10^{-7}), without any appreciable alteration of the tangential growth along the selected planes of growth. Growth from *several* centres may occur due to excessive supersaturation of the main material or to the exceeding of a definite minimum concentration of specific impurities, the latter particularly in the case of crystal growth from the molten state. The formation of macroscopic “single” crystals by growth from several centres, encourages the development of variations of orientation up to strongly marked (“primary”) “block” structures. All the available evidence seems to confirm the fact that in the case of the purest materials and slowest rates of growth and also for growth from the molten state, fundamentally tangential growth occurs. Further complications in crystal growth are caused principally by spatial or temporal variations in the material available during growth, in which impurities may again have considerable effect.

* “Structure-Sensitive Properties,” *loc. cit.*, Sections 7 and 8.

† See the recrystallization results of H. G. Müller, *Phys. Z.* 35, 646 (1934).

‡ A. Smekal, *Phys. Z.* 35, 643 (1934), also “Structure-Sensitive Properties,” *loc. cit.*, Section 9.

(2.3) *Laws of primary crystal flaws*

The deviations from the ideal lattice during the growth of a crystal—gaps, variations in orientation, incorporated foreign atoms—we may call “primary” crystal flaws. In the case of growth from a single centre from material of constant composition both in space and time, the number and distribution of these flaws are determined by the rate of deposition, the temperature and the individual properties of the material of the crystal and of the impurities present. According to (2.2) *the spatial distribution of the flaws is statistically ordered along the principal planes of growth*. The number of flaws in general increases with the rate of growth and with temperature. If these factors are constant, the number of flaws in the same type of lattice is smaller the greater the lattice energy, and for ionic crystals therefore the greater the valency of the components*. The development of flaws is therefore *under attainable conditions of crystallization* for macroscopic three-dimensional crystals to be considered as just as fundamental a property of the crystalline state as the Brownian molecular motion is of gases and liquids; the flaws can in a sense be considered as a “frozen Brownian motion.” The most important flaws seem to be due to incorporated foreign atoms, especially in crystals with maximum lattice energy (diamond, carborundum); in these substances, the fewest flaws are to be expected in crystals of those materials, for which the strongly unsymmetrical nature of the lattice favours the incorporation of the most diverse impurities in the form of solid solutions, e.g. certain silicates (mica). On the other hand, impurities may in special cases, by stopping most of the possibilities of growth, lead to a very perfect “two-dimensional” crystal growth, from which variations of orientation are practically excluded†.

(2.4) *Laws of secondary crystal flaws*

The result of any alteration in the primary flaws or the formation of new flaws in an already developed crystal will be referred to as “secondary” crystal flaws. Two of the simplest cases are of special importance:

(a) Alteration of the temperature from that of crystallization has the following effects: (a 1) Distortion in the neighbourhood of incorporated foreign atoms *not forming solid solutions*, as a result of thermal expansion of the lattice; these lead either (a 1.1) to local inclusions by self-diffusion or (a 1.2) to local development of mechanical cleavage-, slip- or twinning-planes. (a 2) Supersaturation of the lattice structure with regard to the foreign atoms included as solid solutions; the lattice distortion produced in this way is due to flaws caused by the segregation of the superfluous foreign atoms locally along mechanical cleavage-, slip-, or twinning-planes.

(b) By intentional or unintentional mechanical effects (e.g. mechanical working, cleavage) local cleavage-, slip-, or twinning-planes are formed, and possibly also

* “Structure-Sensitive Properties,” *loc. cit.*, Sections 8 and 9.

† For more detailed information on this question, see “Structure-Sensitive Properties,” *loc. cit.*, Sections 9 and 23 (c).

slip- or twin-bands running right through the crystal. According to all the evidence, such phenomena are always associated with the development of flaws, distributed along slip zones of finite thickness. At the same time many complications may also occur, with which it is not possible to deal here in greater detail*.

Special attention must be called to the fact that the flaws formed as in (a 1.2) and in (b) on mechanical cleavage-, slip-, and twinning-planes change in time, even at the temperature of origin and more easily at higher temperatures, by the self-diffusion of particles; which in the case of primary flaws can only occur in materials with very high rates of self-diffusion. The number of newly formed secondary flaws is regularly connected with the intensity of the causative influence. Since the mechanical cleavage-, slip-, and twinning-planes coincide with the planes of the crystal described in (2.2) as the principal growth planes†, *the secondary flaws are statistically arranged about the same planes as the primary flaws.*

(2.5) *Distinction between primary and secondary crystal flaws*

Whilst primary flaws are characterized in general by their amicroscopic dimensions, secondary flaws may reach such a size as to permit of resolution under the microscope, or even occasionally of macroscopic visibility. Direct conclusive information as to the existence of primary flaws is as stated in (2.4) only possible at the crystallization temperature; indirectly of course, evidence of the presence of insoluble impurities at any temperature is sufficient. The presence of flaws of a size visible under the microscope at temperatures well below that of crystallization always affords good reason to suspect their secondary origin; this can be proved with certainty by observing changes in the flaws, on heating up to the crystallization temperature.

(2.6) *Layer, block and mosaic structures*

The complete application of the foregoing criteria to the hitherto observed regular layer, block and mosaic structures has not yet been carried out in all important cases. The suspicion on general grounds of the secondary nature of these "empirical" structures can however be brought forward as evidence in the case of the mosaic structure of NaCl and the twin-band structure of KClO₃ crystals. The familiar behaviour of impurities segregated later is observed for the etching properties of Goetz's block structure in bismuth and in the layer structure of zinc, and according to (a 2) implies their origin as in (2.4); the presence of foreign atoms, introduced intentionally, along pseudo-octahedral planes of bismuth has been proved by Goetz and his collaborators by magnetic and radioactive methods. Also the layer structure found by Straumanis in hexagonal metals (Zn, Cd) involves the incorporation of foreign atoms. Finally it should be emphasized that none of these

* "Structure-Sensitive Properties," *loc. cit.*, Sections 10 and 12.

† "Structure-Sensitive Properties," *loc. cit.*, Section 23 (a).

structures possesses exact regularity, but that they rather show only the expected "statistical ordering"*.

§ 3. CRYSTAL FLAWS AND STRUCTURE-SENSITIVE PROPERTIES

If there is a causal relationship between crystal flaws and the structure-sensitive properties of crystals of a material in the sense of (1.4), then the following very simple conclusions as to those properties which depend on a *large* number of flaws may be drawn:

(a) Different conditions of crystallization give crystals which differ in their structure-sensitive properties, and so provide *proof* of their structure-sensitivity [variation of distribution of flaws as in (2.3)].

(b) The structure-sensitive properties of different individual crystals agree with each other if the conditions of crystallization are kept constant [similarity of primary flaw distribution as in (2.3)].

(c) Similar agreement to that in (b) is shown by crystals with exactly the same conditions of crystallization and previous history [similarity of secondary flaw distribution as in (2.4)].

(d) The structure-sensitive properties of the same crystal can be altered in a regular manner by thermal or mechanical influences, so that the structure-sensitivity even in a single individual is demonstrable [difference between primary and secondary flaw distribution as in (2.4)].

(e) If variation in the structure-sensitive properties is caused by the heat-treatment of crystals with isotropic thermal expansion and not subjected to mechanical treatment, this is due to the effect of foreign atoms [alteration of flaws due to foreign atoms as in (2.4), (a) without other secondary effects].

On account of their dependence on causes which follow *statistical* laws, the numerical values of the structure-sensitive properties of different individual crystals will in general be somewhat different and will possess definite characteristic *frequency distributions*. Consequently we have the following:

(f) The average fluctuation of a structure-sensitive property is smaller the more flaws are causally active and the more similar flaws are available for this purpose.

(g) If a structure-sensitive property depends only on one or a few flaws, large variations in its value may occur.

II. RESULTS FOR SALT CRYSTALS

§ 4. EXPERIMENTAL PECULIARITIES OF SALT CRYSTALS

At the time when our experimental work on the questions dealt with above was begun, researches of a different nature had already been undertaken by several workers on metal crystals. The chief reasons why we selected salt crystals were:

* "Structure-Sensitive Properties," *loc. cit.*, Section 10. The super-lattice interference effects to be expected according to Zwicky as in (1.6) in the case of a perfectly regular secondary structure, have not been observed in any case.

(a) the completeness of the theoretical knowledge of the ideal simple ionic lattice; (b) the ease of preparation of salt crystals from a melt and the existence of natural crystals grown nearly at room temperature; (c) the optical check provided by the transparency of salt crystals, as to the intentional or unintentional introduction of foreign atoms; (d) the fact that self-diffusion can be measured by means of the ionic conductivity; (e) the relatively great brittleness and distinct plasticity of salt crystals; (f) the optical and thermal isotropy; (g) the possibility of detecting primary crystal flaws and their alteration due to external influences by photochemical and photoelectric methods (see § 5). So far as is known, no other group of substances unites in itself even approximately as many advantages, as a comparison with the later work of Goetz and his collaborators on bismuth crystals will show. With regard to their structure-sensitive properties, salt crystals are at present the best understood class of crystals, although even here many questions require further work before they can be answered. It is impossible in the following to give a complete survey of present knowledge of the subject*.

We restrict ourselves therefore to results which for fundamental reasons cannot up to the present be obtained from other substances and which are primarily related to the possibility of detecting primary and secondary structural flaws in crystals.

As far as the *general* structure-sensitive properties and their relation to structural flaws are concerned, it would be expected from the reasons set out in the theoretical section that the results should apply also to crystalline materials of any class.

§ 5. DETECTION OF STRUCTURAL FLAWS IN SALT CRYSTALS

(5.1) *Wave mechanical basis of photochemical properties of crystals*

According to the wave mechanics of crystal lattices, a locally fixed electron-binding is impossible in the interior of either a finite or an infinite lattice; on the other hand, it is possible at the internal and external surfaces and (what is practically the same thing) also at and in the immediate neighbourhood of foreign atoms which are not present in the form of a solid solution†.

In non-conducting salt crystals, therefore, *flaws in the crystal structure are characterized by locally fixed electron binding*, and can be investigated by means of the particular absorption spectrum of these bindings. Fundamentally, all the (anionic) particles located at structural flaws can be detected by absorption measurements, their concentration relative to the whole number of particles being of the order of 10^{-4} to 10^{-7} . Further, the marking of *definite* flaws in crystal structure is only made possible by the fact that locally fixed electron-bonds can exist solely where there are structural faults; a local metastable excitation of the elements on the inner surface is necessary to secure sufficiently lasting marks without permanent local destruction of the structure of the crystal. In salt crystals, this is attained by the

* The majority of the relevant papers are dealt with in "Structure-Sensitive Properties" (*loc. cit.*), to which we refer in particular for low temperature self-diffusion.

† "Structure-Sensitive Properties," *loc. cit.*, Section 10 (c). See also A. Smekal, *Phys. Z.* 35, 363 (1934).

photoelectric ejection of the electron from an anion in the flaw, and its photochemical union with a neighbouring cation of the flaw, so that two neutral atoms are formed locally, the absorption spectrum of these atoms making it possible to deduce the number, space-distribution, stability and effectiveness of the structural flaws so marked.

(5.2) *Photochemical marking of amicroscopic structural flaws in rock-salt*

The procedure described above has been applied to the various alkali halides and to fluorspar. In the particular case of rock-salt, it corresponds to the amicroscopic yellow coloration discovered by Goldstein in 1896 on irradiation with short-wave ultra-violet light*, which is due to separated sodium atoms, and possesses an easily measured absorption band in the blue. Electrons are photoelectrically ejected from the sodium atoms by absorption in this band, and after longer free paths, separated chlorine atoms can finally† revert to ions, so that the original uncoloured state of the crystal is restored‡.

All processes for the production of such colours which are not, or are not purely, photochemical (coloration by adding alkali or alkaline earth vapours, by electron bombardment, or by irradiation with cathode rays, X-rays or radium rays) are demonstrably connected with secondary alterations of the structural flaws marked, which in general still remain after the decoloration of the crystal‡. It is easy to convince oneself experimentally by this method that colouring a crystal really depends on locally fixed electron bindings.

(5.3) *Detection of ultra-microscopic structural faults*

The photochemical colours are sensitive to heat. If they are replaced by additive colours of sufficient intensity, stable under heat treatment, then the sodium atoms, which are responsible for the coloration, are caused by moderate heat treatment to coagulate into particles detectable by the ultra-microscope. In many cases the particles are arranged in the interior of the crystal along plane or curved intersecting surfaces, so that an otherwise undetectable internal crack system of the crystal is made accessible to microscopic investigation. After internal vaporization and further coagulation, the same ultra-microscopic distribution is obtained, thus proving the definitely localized nature of the crack system§. The demonstration of such crack systems, occurring predominantly in imperfect crystals, by means of the amicroscopic colours from sodium atoms, gives an independent proof that the amicroscopic colours also are associated with structural flaws, as required by the theory|| (5.1).

* A. Smekal, *Wien. Anz.* p. 195 (1926); *Proc. Int. Congr. Phys., Como*, 1927, 1, 181 (Bologna, 1928); *Proc. 8th Int. Congr. of Photography, Dresden*, 1931, p. 34 (Leipzig, 1932); *Phys. Z.* 33, 204 (1932).

† For the possible intermediate processes, compare Section 10 (b), "Structure-Sensitive Properties," *loc. cit.*

‡ The photochemical detection of changes in secondary flaws has been very thoroughly treated by H. J. Schröder, *Z. f. Phys.* 76, 608 (1932); and K. Helbig, *Z. f. Phys.* 91, 573 (1934).

§ E. Rexer, *Z. f. Phys.* 75, 777 (1932); 76, 735 (1932).

|| A. Smekal, *Proc. 8th Int. Congr. of Photography, Dresden*, 1931, p. 34 (Leipzig, 1932).

§ 6. CRYSTAL STRUCTURE AND PHOTOCHEMICAL COLORATION

(6.1) *Structural sensitivity due to structural flaws*

If the photochemical coloration of rock-salt crystals is investigated under the action of the same number of quanta of ultra-violet light, the coloration being measured by the height of the absorption band at room temperature, then the following results are obtained:

(a) Crystals which are produced under different conditions, give different colorations.

(b) Crystals made under exactly corresponding conditions, give exactly the same coloration.

(c) Crystals prepared in a similar way and with the same history likewise give the same coloration.

(d) The capacity for coloration of a crystal is systematically increased by mechanical treatment.

(e) Purely thermal treatment similarly produces a regular change in coloration.

We see that the photochemical coloration of rock-salt is a structure-sensitive property, and complies in fact with the very simple laws required by § (3), (a) to (e) for a property conditioned by faults of crystal structure.

We have found that the same laws also apply to the structural flaws which are directly demonstrated by the ultra-microscope in the manner explained in (5.3). By the method mentioned, it has been proved conclusively that the photochemical coloration is connected directly with the primary and secondary structural flaws in rock-salt, and that in them, according to (e) and § 3 (e), foreign atoms play an important part*.

The latter fact receives further confirmation from the increasing capacity for coloration in synthetic rock-salt crystals with increasing quantities of insoluble impurities†.

(6.2) *Distribution and properties of flaws*

According to (5.1), all particles on the inner surface of a crystal can be identified by optical and photochemical methods. That these particles are present in a definitely limited number is shown according to (5.1) not only by the optical method for the uncoloured crystal, but also from the approach to a definite photochemical colour saturation when the ultra-violet irradiation is continued indefinitely. From the time rate of coloration and of decoloration, or from repeated coloration and decoloration, it is generally possible to deduce the nature and stability, as well as the spatial distribution of the flaws in the crystal‡. It is found

* At a purity of 99.99 per cent to 99.995 per cent of NaCl, the number of foreign atoms and the optically determined number of structural-flaw cations are of only slightly different orders of magnitude.

† Cf. A. Smakula, *Gött. Nachr.* p. 110 (1929); R. Hoffmann, *Z. f. Phys.* **94** (1935); A. Smekal, *Phys. Z.* **35**, 643 (1934).

‡ The photochemical detection of changes in secondary flaws has been very thoroughly treated by H. J. Schröder, *Z. f. Phys.* **76**, 608 (1932); and K. Helbig, *Z. f. Phys.* **91**, 573 (1934).

that the flaws are neither of the same type nor arranged at equal distances, so that with reference to these two factors, there is a definite distribution of flaws for each crystal. The very close accordance between the colours of different parts of a synthetic crystal is due to the very great number (e.g. 10^{16} per cm^3) of colouring atoms, and the identity of distribution properties of the flaws indicated by these atoms. If, however, *just as many* colour-atoms are produced in similar crystals through *different* colouring and decoloration operations, then the difference in the time-rates of their decoloration shows that different distributions of flaws are indicated. It has been shown by similar experiments using heat treatment or mechanical working that the secondary flaws so produced (see (2.4)) are in a markedly unstable condition, and only after a considerable time is a quasi-stationary behaviour reached, consequent on rearrangement of the elements on the internal surfaces*.

§ 7. MACROSCOPIC STRENGTH LIMITS OF SALT CRYSTALS

(7.1) *Structure sensitivity of macroscopic strength-properties*

It was emphasized in (1.1) that the strength properties of all materials are structure-sensitive. We have shown by a series of detailed experiments that for natural and artificial rock-salt crystals and for other alkali halides, the very simple laws set out in § 3 (a) to (e) *for a property of crystals determined by flaws, are fulfilled at all temperatures*. It is to be specially noted that the strength properties are markedly dependent on the thermal history of the material of the crystal, and that therefore the flaws due to admixture of foreign atoms are concerned in a considerable degree.

Artificial crystals with increasing quantities of insoluble foreign atoms introduced, show regular corresponding changes in strength. For simplicity we confine ourselves in the following to the limits of cohesion and of plasticity under simple tension or compression.

(7.2) *Macroscopic cohesion of crystals*

The experimental separation of cohesion and plasticity is obtained for rock-salt on cooling to low temperatures†. From about -200°C . downwards, rock-salt crystals may be regarded as brittle, so that at these temperatures they are similar to the numerous brittle inorganic crystals. The tensile strength is independent of the cross-section of the crystal and thus measures the macroscopic *cohesion* of the crystal; it is almost independent of temperature and amounts for the purest synthetic crystals, perpendicular to the cube faces, to about 600 gm./mm^2 , with a mean deviation of ± 6 per cent. This cohesion limit is systematically reduced on the introduction of increasing quantities of insoluble foreign atoms, or by mechanically produced distortion‡. With increasing temperature, the ultimate strength first shows

* K. Helbig, *loc. cit.*

† A. Smekal, *Z. f. Phys.* **83**, 313 (1933); *Phys. Z.* **34**, 633 (1933).

‡ W. Burgsmüller, *Z. f. Phys.* **80**, 299 (1933); **83**, 317, 321 (1933).

a fall to a minimum (200 gm./mm²) at about room temperature, and later rises steeply to a maximum ($> 10,000$ gm./mm²) in the neighbourhood* of 650° C.

Since this and all the related peculiarities are connected with the occurrence of crystal *plasticity*, which changes the single crystal into a polycrystalline aggregate, we shall only deal in detail with the *commencement* of plasticity.

(7.3) *Macroscopic elastic limit*

The stress which produces any fixed small plastic extension decreases smoothly with rising temperature. However, it is quite impossible to determine the “true” commencement of plasticity by any limiting extension defined in this or a similar way. If we define as the “limit of elasticity,” that stress at which the first permanent changes within the crystal are detectable, then in general the results will still depend on the sensitivity of the technique employed. If we employ however the properties most sensitive to structure, then we may hope to arrive at lower critical stresses than those that can be determined up to the present. We first investigated this limit carefully at room temperature, and found that by means of the double refraction due to stress† or by means of ionic conductivity‡ we obtained low limiting stresses, but that the determination of a “photochemical limit of elasticity” was the most sensitive method§.

There are here in a noteworthy way two methods which give concordant data: the external stress is determined, above which the tendency to photochemical coloration (§ 6) of an uncoloured crystal increases, and at which a coloured crystal experiences a decoloration||. For the purest unannealed synthetic rock-salt crystals, this photochemical limit of elasticity is 37 gm./mm², at room temperature, for compression perpendicular to the cube faces of the crystal. Crystals with insoluble foreign atoms (SrCl₂) in the lattice yield exactly the same stress, independent of the content of impurity¶.

The “yield point” determined in compression or tension from the striations due to slip bands on the surface, or from the appearance of the first complete slip planes of the crystal as recognized by double refraction under stress, is, on the other hand, about 150 gm./mm² for the pure crystal, and shows a steep increase with increasing content of foreign atoms**.

(7.4) *Plastic deformation on slip planes*

The first permanent alterations in the interior of a deformed crystal, according to the foregoing, are of a local nature, since the first complete slip planes recognizable by an external change of form occur at a higher stress. Optical stress measure-

* W. Burgsmüller, *loc. cit.*; W. Theile, *Z. f. Phys.* 75, 763 (1932); D. Mahnke, *Z. f. Phys.* 90, 177 (1934).

† W. Schütze, *Z. f. Phys.* 76, 135 (1932).

‡ M. Kassel, *Z. f. Phys.* 90, 287 (1934).

§ H. J. Schröder, *Z. f. Phys.* 76, 608 (1932); E. Poser, *Z. f. Phys.* 91, 593 (1934).

|| A. Smekal, *Wien. Anz.* 22, 46 (1927); H. J. Schröder, *loc. cit.*

¶ E. Poser, *loc. cit.*

** A. Edner, *Z. f. Phys.* 73, 623 (1932); H. Schönfeld, *ibid.* 75, 442 (1932); W. Metag, *ibid.* 78, 363 (1932); W. Klemm, *ibid.* 94 (1935).

ments on potassium halides* have explained the intermediate phase as the *formation of local limited slip planes*†, which spread with increasing stress, and finally develop into complete slip layers. In the presence of several crystallographically equivalent slip planes, this pre-growth favours chiefly the slip planes, in the direction which is that of the shortest length within the crystal; this preference is actually observed in artificial rock-salt crystals, and still remains at greater deformations‡. The crystallographic nature of the slip planes produced depends on the relation between the direction of the tension or compression relative to the crystal lattice, as well as on the temperature. In rock-salt, rhombic-dodecahedral, cube and octahedral planes can be slip planes, with the normal to the rhombic-dodecahedral plane as the common slip direction§, whilst the first two mentioned planes can also be cleavage planes. The photoelastic investigations show that the directions of the crystallographic planes merely represent preferred directions, which only agree with the actual slip surfaces within a certain deviation. The origin and course of the actual slip planes are therefore determined by conditions which are not fundamentally crystallographic.

§ 8. STRENGTH PROPERTIES AND CRYSTAL FLAWS

From the experimental data given above (§ 7) and from the results on flaws (§§ 5 and 6) the following relations between the limits of strength and flaws in crystals can be deduced.

(8.1) *Macroscopic cohesion and flaws in crystals*

Macroscopic crystal cohesion is in general *diminished* by increase of flaws (7.2). The greatest observed diminution, to a quarter of the cohesion of the purest crystal, was produced by a two- to fourfold increase of the flaws. We conclude from this that the cohesion of rock-salt is determined by a *large* number of flaws, which however in view of the considerable dispersion of the experimental results cannot all be distributed in the same way; in fact it has been shown that the formation of the breaking surface mainly proceeds from the surface of the crystal||. A diminution of the macroscopic cohesion by the concentration of stress at hollow flaws is theoretically explicable without difficulty, and is reconcilable also with the theory of the ideal lattice, according to which at the moment of breaking at the critical flaws, stress maxima of the order of magnitude of the cohesion in the ideal lattice are to be expected¶. A calculation of the ratio of the two cohesions (600/200,000

* W. Schütze, *Z. f. Phys.* 76, 135 (1932).

† The formation of locally limited slip planes has been definitely shown by ultra-microscopic (§ 5) and by optical stress observations to be related to the thermal action of foreign atoms mentioned in (2.4) under (a).

‡ D. Mahnke, *Z. f. Phys.* 90, 177 (1934), p. 178; A. Smekal, *Z. f. Phys.* 93, 166 (1935).

§ Cf. E. Rexer, *Z. f. Phys.* 75, 777 (1932); S. Dommerich, *ibid.* 90, 189 (1934); H. Wolff, *ibid.* 93, 147 (1935).

|| Cf. H. Schönfeld, *Z. f. Phys.* 75, 442 (1932).

¶ A. Smekal, *Phys. Z.* 26, 707 (1925); 27, 837 (1926); 34, 633 (1933).

to 400,000 gm./mm.²) has not hitherto been possible in regard to the mutual actions of a multitude of flaws*.

(8.2) *Spectroscopic determination of molecular cohesion in crystals*

On account of the gradual nature of the failure in tension, there are at the moment when this commences, so few points of maximum stress, that their experimental investigation seems hopeless. This is not the case with compression, where an immense number of cleavage surfaces are formed. We have found that crystals with flaws which are photochemically marked give a shift of the absorption band of about 95 Å. towards the red, at this limit and at room temperature (3000 gm./mm.² perpendicular to the cube faces)†. This shift is independent of the number of primary flaws, and corresponds to a local increase of energy of 8×10^{-14} ergs. or 0.05 e.V. per colouring atom. In homogeneous elastic strain of the ideal rock-salt lattice, this increase of elastic energy per lattice element corresponds to 300,000 gm./mm.² perpendicular to a cube plane, which agrees extremely well with the cohesion of the ideal lattice (200,000 to 400,000 gm./mm.²). In view of the expectation of the general correctness of the ideal lattice theory given in (1.4), this agreement indeed *verifies the order of magnitude of the actual molecular cohesion given by this theory*‡.

(8.3) *Crystal flaws and photochemical elastic limit*

From the procedure used to determine photochemical elastic limits (7.3) it follows definitely that the *first detectable permanent changes of a crystal on mechanical deformation occur at the flaws*. The destruction of colouring atoms at the photochemical limit of elasticity yields an energy increase of about 2.4×10^{-13} ergs. or 0.15 e.V. per colouring atom, as estimated by photoelectric and thermal methods§. If this quantity of energy due to the coloration is attributed to an ion-pair in the flaws concerned, then we calculate, in a similar way to the above, that at the flaws there are stress maxima of the order of 350,000 gm./mm.² Further, the *commencement of plasticity is thus determined by local overcoming of the ideal lattice cohesion, which spreads out from the positions of these flaws*. The result of this local overcoming of cohesion is in a certain sense observable even in an amicroscopic state, namely by the *increase in the number of flaws*, established by the increasing capacity for photochemical coloration at the photochemical limit of elasticity (7.3). From these facts, it follows that the first changes in flaws must occur in the *flaws of maximum stress*, and that therefore the photochemically determined stress limit actually represents a finite "limit of elasticity." From this it can easily be understood that this limit might be unaffected on artificially adding flaws by introducing foreign atoms: this

* The only partially verified fracture theory of A. A. Griffith on the fracture of glass assumes single cracks growing with the stress, and leads for rock-salt to a depth of the order of 0.5 mm. for the cracks, which is disproved by the fact that the macroscopic cohesion remains unaltered even down to the smallest cross-sections (0.25 mm.²).

† K. Helbig *Z. f. Phys.* 91, 573 (1934); E. Poser, *Z. f. Phys.* 91, 593 (1934).

‡ A. Smekal, *Phys. Z.* 34, 633 (1933); a similar conclusion was reached in *Phys. Z.* 27, 837 (1926).

§ The numerical values quoted in the last-mentioned work are here corrected by means of a recently published determination of the ratio of the photoelectric and the thermal energies required for ionization (A. Smakula, *Gött. Nachr.* p. 55 (1934)).

must occur for flaws whose properties only permit less than the highest stress maxima. The close reproducibility of the photochemical limits of elasticity (± 5 per cent) implies considerable differences of stress maxima in this case, since the experimental determination of the photochemical limit of elasticity demands that there must be permanent changes on at least 5×10^{12} flaws per c.c.

(8.4) *The mechanism of plastic deformation on slip planes*

The preceding results give the *local* and *energy* requirements for the commencement (7.3) and the development (7.4) of plastic deformation, which every applicable theory of plasticity must bear in mind, and which must be linked up with *dynamical* ideas. The observed types of slip plane (7.4) find an explanation purely on energy grounds as *planes of minimum energy of molecular separation in relation to neighbouring directions of the lattice structure*, along which the propagation of stress maxima through the crystal lattice occurs most easily*. The increase of external macroscopic stress required for this follows doubtless partly from the local variations in the inhomogeneity of the distribution of elastic stress at the peaks of stress, and partly from the disturbance of their propagation due to adjacent flaws†. The observed decrease of the elasticity limit and yield point (7.3) with increasing temperature shows further that *heat motion participates energetically in the local overcoming of lattice cohesion, and in the propagation of the stress maxima*. This results from the *influence of the occurrence of high stress maxima on self-diffusion processes within the flaws*: the "energy of separation" of the individual crystal elements is so greatly reduced by the local supply of elastic energy, that their thermal diffusion occurs enormously faster than in a mechanically unstrained crystal; on this account an advance of these stress maxima is possible, which can lie further behind those corresponding to the cohesion of the ideal lattice, the higher the temperature‡. It seems possible§ that such molecular processes, with a slip direction as preferred direction, represent the *fundamental phenomena of plasticity* and cause slip within flawless regions of the lattice; molecular diffusion processes of this kind possess the characteristic dependence on time and non-crystallographic nature of macroscopic plasticity processes, whilst their fundamental reduction at low temperature yields the increasing brittleness (7.2) found here. It is satisfactory that the recent plasticity theory of G. I. Taylor|| has adopted many parts of this earlier work in its basis. As far as I can see, this theory is only in serious disagreement with experience—in relation to the commencement of plasticity and the nature of

* A. Smekal, *Phys. Z.* **34**, 633 (1933); "Structure-Sensitive Properties," *loc. cit.* section 23 (a), table 19 and section 20 (d).

† The statistical arrangement of flaws about the slip planes which coincide with planes of slowest growth as given in (2.3) and (2.4) is consequently important for the macroscopic strengthening of the crystal.

‡ The qualitative explanation of the temperature-dependence of plasticity due to this cause was stated by A. Smekal, *Phys. Z.* **34**, 633 (1933), and later in a form differing only in externals by E. Orowan, *Z. f. Phys.* **89**, 605 (1934), who dealt in detail with the yield points in metal crystals.

§ A. Smekal, *Phys. Z.* **34**, 633 (1933); "Structure-Sensitive Properties," *loc. cit.* section 23 (a), table 19 and section 20 (d).

|| G. I. Taylor, *Proc. R. S. A.*, **145**, 362, 388 405 (1934).

“hardening”—where its assumptions are different from the above general results. By the direct measurement of molecular crystal cohesion on single atomic particles of the crystal flaws, it seems in any case to have been shown with certainty, that the effect of flaws in combination with the theory of the ideal lattice must be taken into account for an understanding of macroscopic strength properties of crystals.

DISCUSSION

Dr C. H. DESCH. The evidence for a secondary structure in crystals is not derived from any single property, but is cumulative. Among the facts which lend a strong support to the hypothesis are those concerning the attack of solvents on crystals. That etch-figures arise either from impurities or from convection currents has been disproved, and the regularity of their distribution on uniform crystal faces indicates a periodic structure. The dimensions found for bismuth by Goetz require a unit of 1.4μ , whilst Belaiew's pits in α -iron give a cube of 0.25μ side. In other crystals the unit may perhaps be several microns. A dodecahedral face of a tin crystal gives long parallel ridges on etching, and these ridges are crossed by markings approximately 2μ apart. Silicon iron gives a coarser pattern, which corresponds very closely with the magnetic pattern recently found by McKeehan to be given by a colloidal suspension of ferric oxide on a magnetized silicon iron crystal. The facts that on deformation slip occurs only on planes many thousands of atoms apart, and that the behaviour of metals on melting and of certain non-metallic substances, such as arsenious oxide, on solution in water, points to the survival of small blocks of the same order of magnitude for an appreciable time, lead to a similar conclusion. The papers read at this Conference make it clear that there is as yet no satisfactory proof of the origin of a secondary structure on this scale, but whatever its theoretical basis, practical experience clearly indicates its existence.

Prof. E. N. da C. ANDRADE. Some experiments carried out by Mr J. G. Martindale and myself throw light both on the stability of the crystal lattice and on the question of faults in crystals, discussed by Prof. Smekal. Thin films of metal, in particular of gold and of silver, were deposited on various surfaces by cathodic sputtering. The surfaces were very carefully cleaned before deposition, and conditions were chosen so as to give very uniform and reproducible films. Particular care was taken to avoid any heating of the films during sputtering. After preparation the films were heated *in vacuo* at various temperatures between 230° and 600° , and the modifications produced were studied microscopically, up to very high magnifications. The microscopic method is inferior to the electron diffraction method in that it gives no direct information as to the spacing of crystal planes, but, on the other hand, it gives information as to local variations of structure and as to crystal boundaries, which the electron method cannot supply. This information can be supplemented by the use of polarized light.

The films, which were about 50 atoms thick, appeared, before heating, perfectly homogeneous under the highest magnification. After heating at 230° C. for an hour

or two the film appeared unchanged to the eye, but under the microscope small specks, varying from about 0.5 to 3μ in diameter, were seen. These, examined in parallel plane polarized light between crossed Nicols, showed as white discs with a black cross superimposed, reminiscent of the rings and cross figure observed with uniaxial crystals in convergent polarized light. The appearance is shown in figure 1, where the magnification is $\times 5000$. The arms of the cross are parallel to the planes of the analyzing and polarizing Nicols, and rotate with the Nicols; while rotating the specimen leaves them at rest. This is the known optical behaviour of spherulites, which are spherical masses of fibres of birefringent crystal, arranged radially. The resolution is not sufficient to enable us to decide that the mass is actually spherical—it might be a cone-shaped mass of radiating uniaxial fibres, or a hemisphere. We have here evidence for crystalline fibres radiating from a centre, and that these fibres are birefringent, which is remarkable since both gold and silver, with which the phenomenon was observed, are cubic. The formation of these centres is independent of the surface, and has been obtained with ordinary glass, fused quartz glass, the natural faces of diamond crystals and mica, and also at the free edge of a film, which shows that it is not due to strain. These spherulitic particles have even been obtained on top of a flat silver crystal, by heating a film laid down on top of a first film, which had already been crystallized by prolonged heating.

Further heating, especially at a higher temperature, leads to a growth of the particles, but as they grow they lose their birefringence. The black intersection of the two arms of the cross increases in size, and finally we are left with a well formed cubic crystal, with its (111) face on the glass or crystal surface. Such crystals, which can be grown to sizes from 4μ to 15μ across, show birefringence at the extreme edge only. Any particles which do not grow, retain their spherulitic character: any that do, lose it. It would therefore appear that, under the conditions of these experiments, at any rate, the cubic lattice is not stable for particles below 3μ or so across. The effect is illustrated in figures 3, 4, 5, 6, which show stages of growth in a silver film on silica glass, after successive heatings.

In these crystallizations from the films, the crystalline aggregates are formed very slowly. Another way in which small particles can be formed slowly is by reduction of a solution of the metallic salt in silicic acid gel. Gold particles 1 to 2μ in diameter were prepared by reducing gold chloride in the gel with either sodium sulphite or oxalic acid. These particles, when washed clean and examined in parallel polarized light, showed the same birefringence as the crystalline aggregates in the films, as illustrated in figure 2.

It seems unlikely that a few atoms can maintain themselves in a cubic lattice—clearly less than 8 cannot, and even with 10^2 or 10^3 times this number there will probably be a tendency to form a spherical aggregate. In the light of these experiments it is suggested that the first stage of crystallization is the formation of such an aggregate, on which many flat ordered faces eventually appear, so that the form is polyhedral. From these faces, columns of ordered atoms grow out, which have an approximately cubical structure, but owing to the relatively small width of the columns, or fibres, compared to the length, the structure is tetragonal, with a small

difference of axial ratio. This would seem to be plausible in view of Lennard-Jones' calculations of the different stable spacing in a plane lattice, and in a cubic

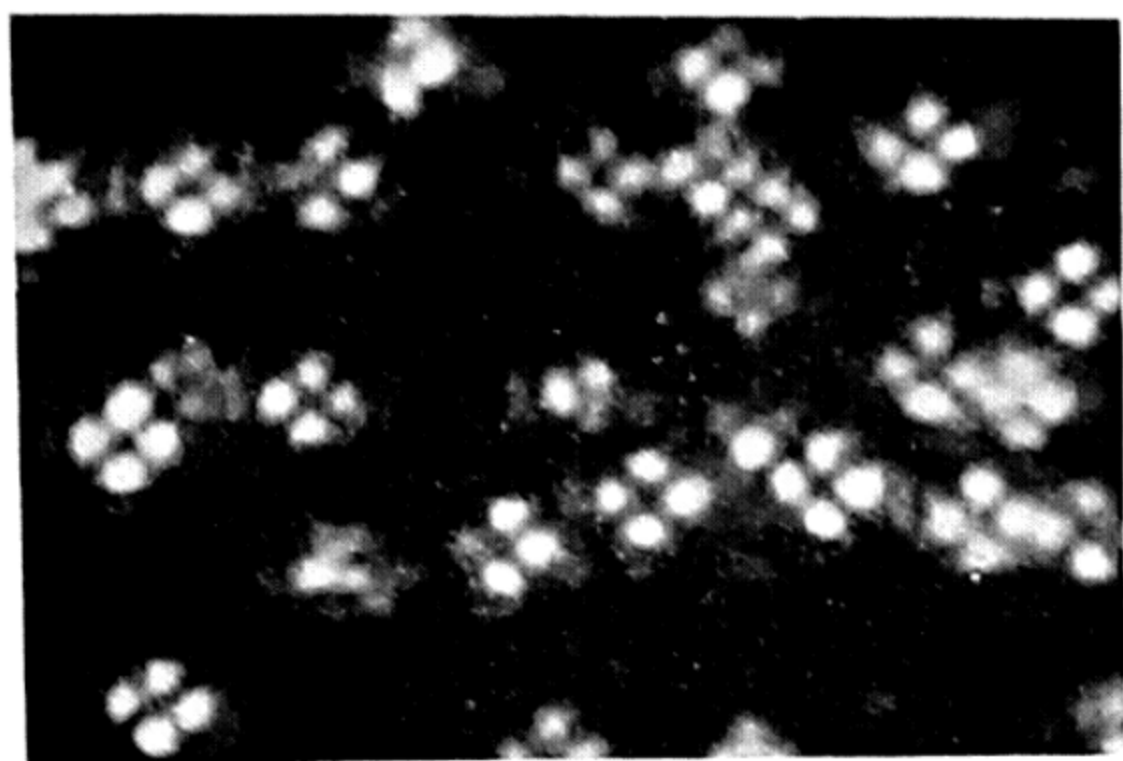


Figure 1. Particles on heated film ($\times 5000$)

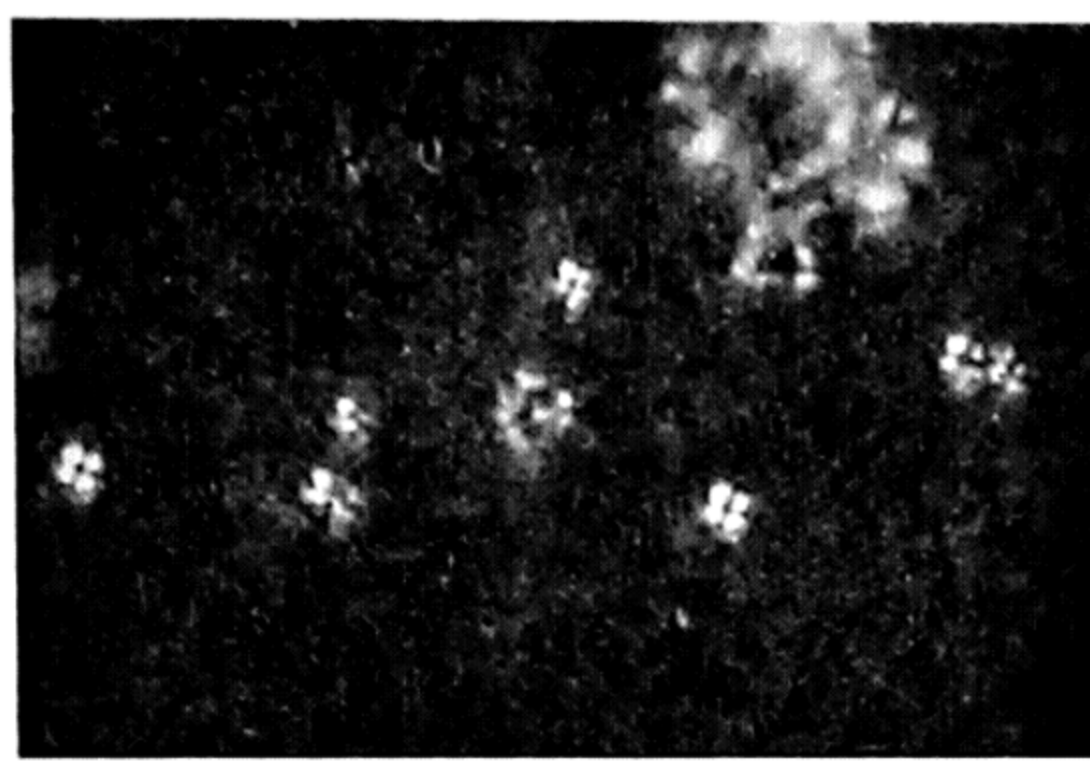


Figure 2. Particles formed in silica gel ($\times 1650$)

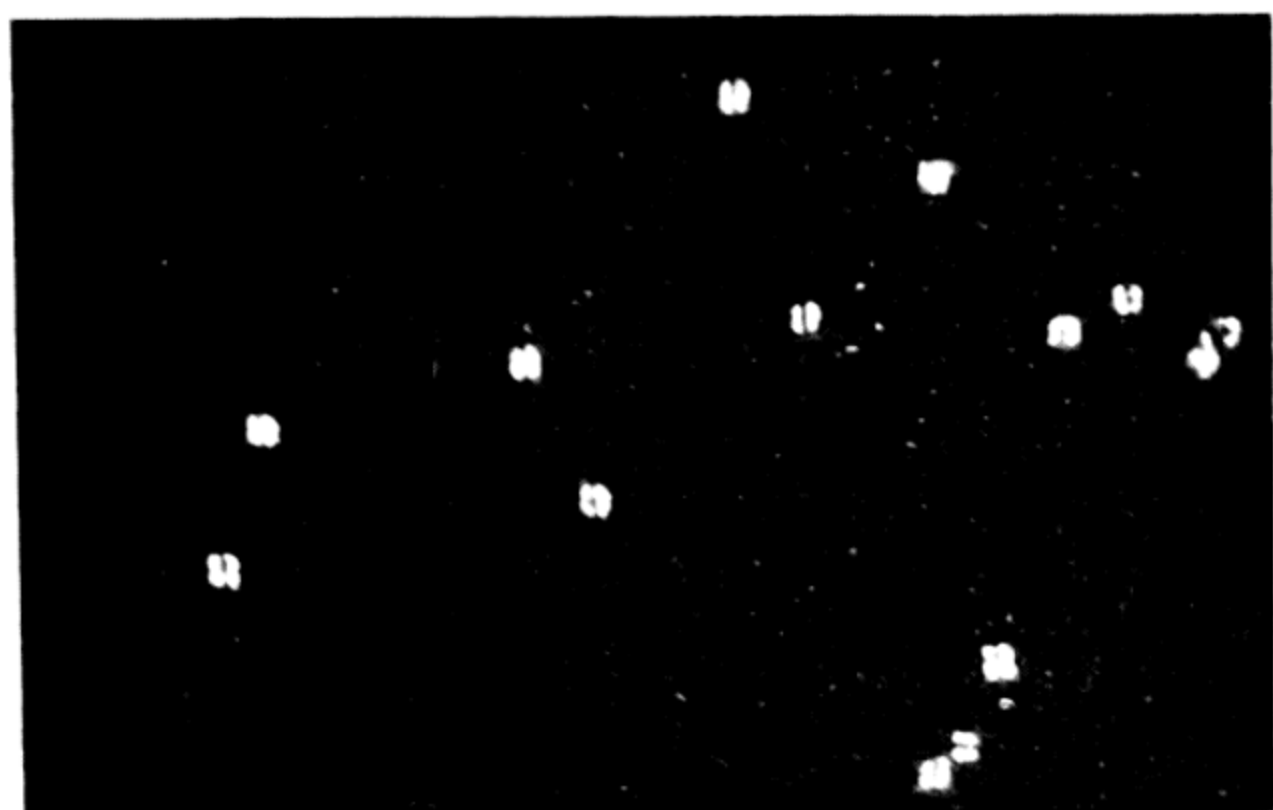


Figure 3



Figure 4

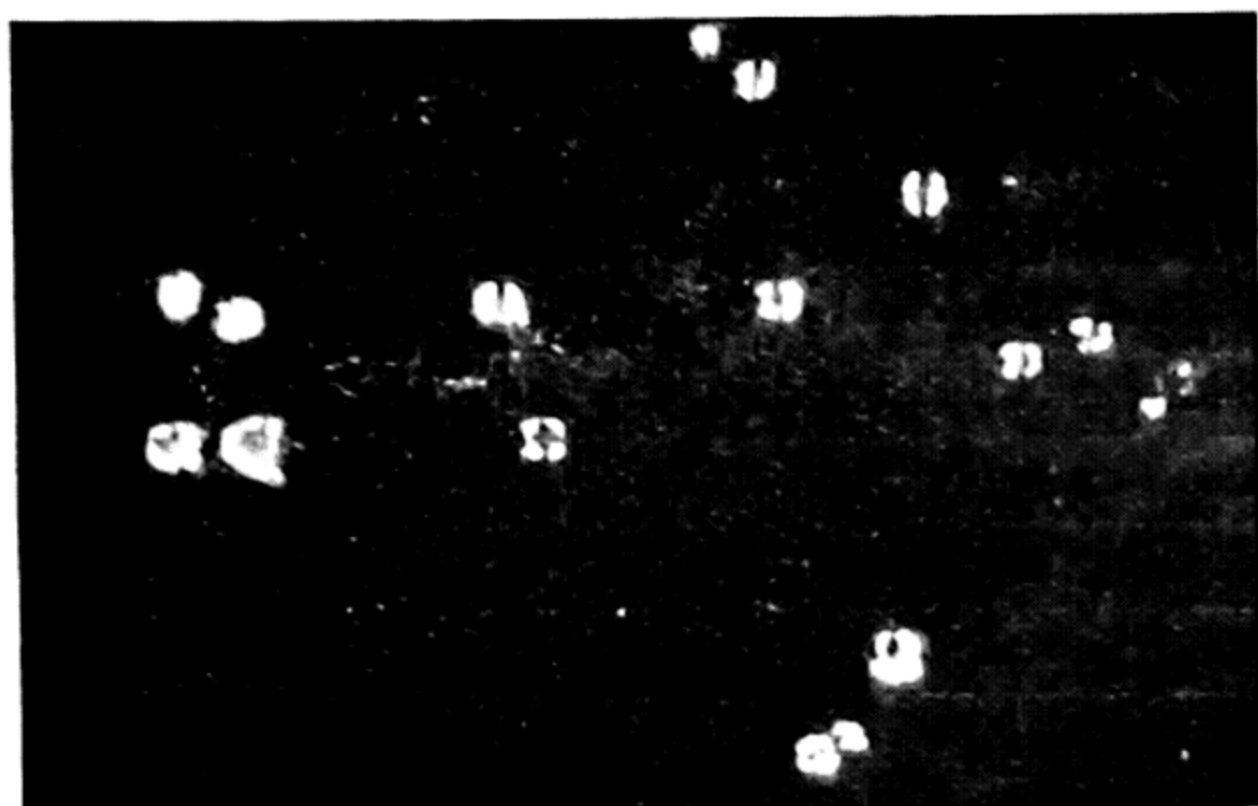


Figure 5

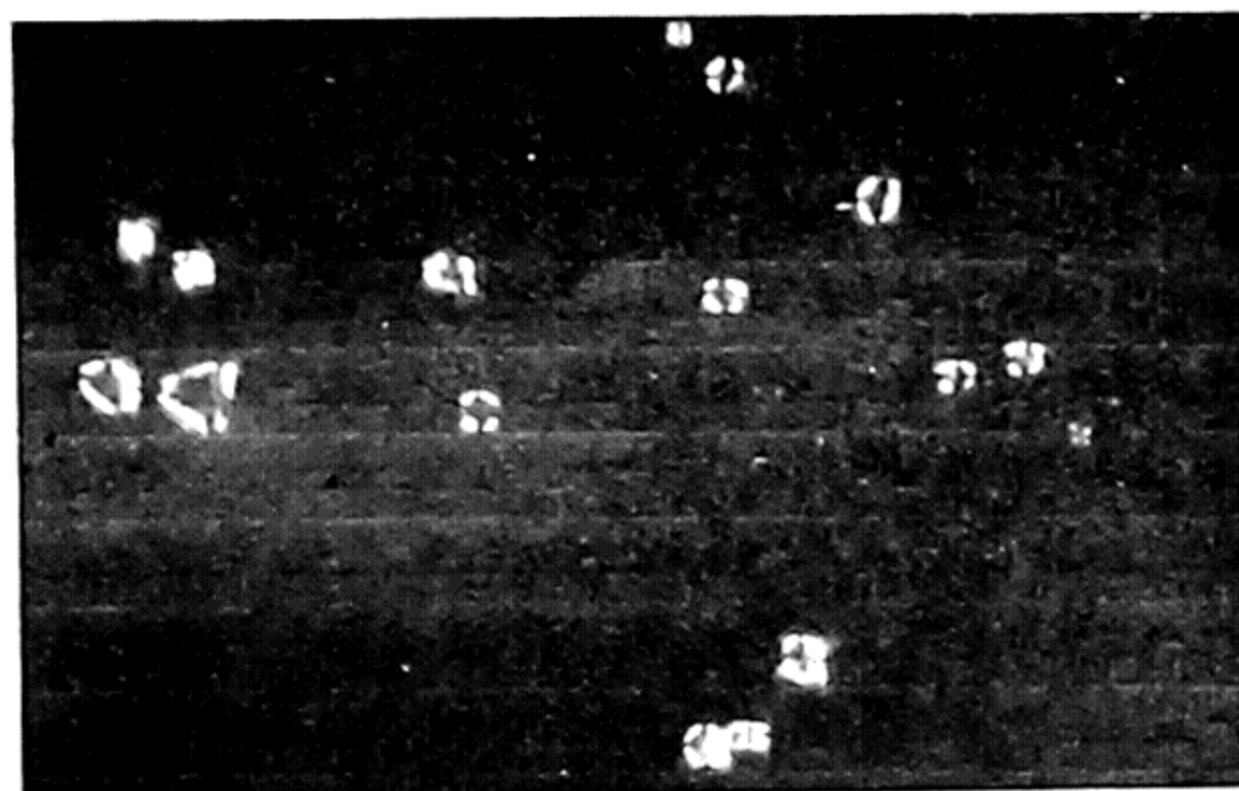


Figure 6

Figures 3-6. Successive stages of growth of particles on heating ($\times 850$)

lattice, the tendency, in the case of particles between which van der Waals' forces prevail, being for a wider spacing in the former state. When the number of planes is relatively few and their dimensions are also restricted, some tendency to the wider spacing should persist. As the total width of the spherulitic particles is only a few

thousand atoms, the single fibres may reasonably be supposed to be only a few tens of atoms across, and a few thousand atoms long. If these tentative suggestions are correct the birefringence is explained.

Since prolonged heating never converted a small spherulite to cubic form it would appear that the ideal lattice is not stable for cubical metals below a certain size.

The other aspect of the work to which I wish to direct attention deals with effects produced by the surface on which the film is sputtered. With films prepared on glass surfaces (quartz glass or microscope cover-slips) the crystallites (spherulitic aggregates) showed a tendency to form up in well-defined lines, as illustrated in figure 7. Control experiments showed that these were not due to polishing scratches. To see if the lines could be due to surface impurities the metal film was removed,

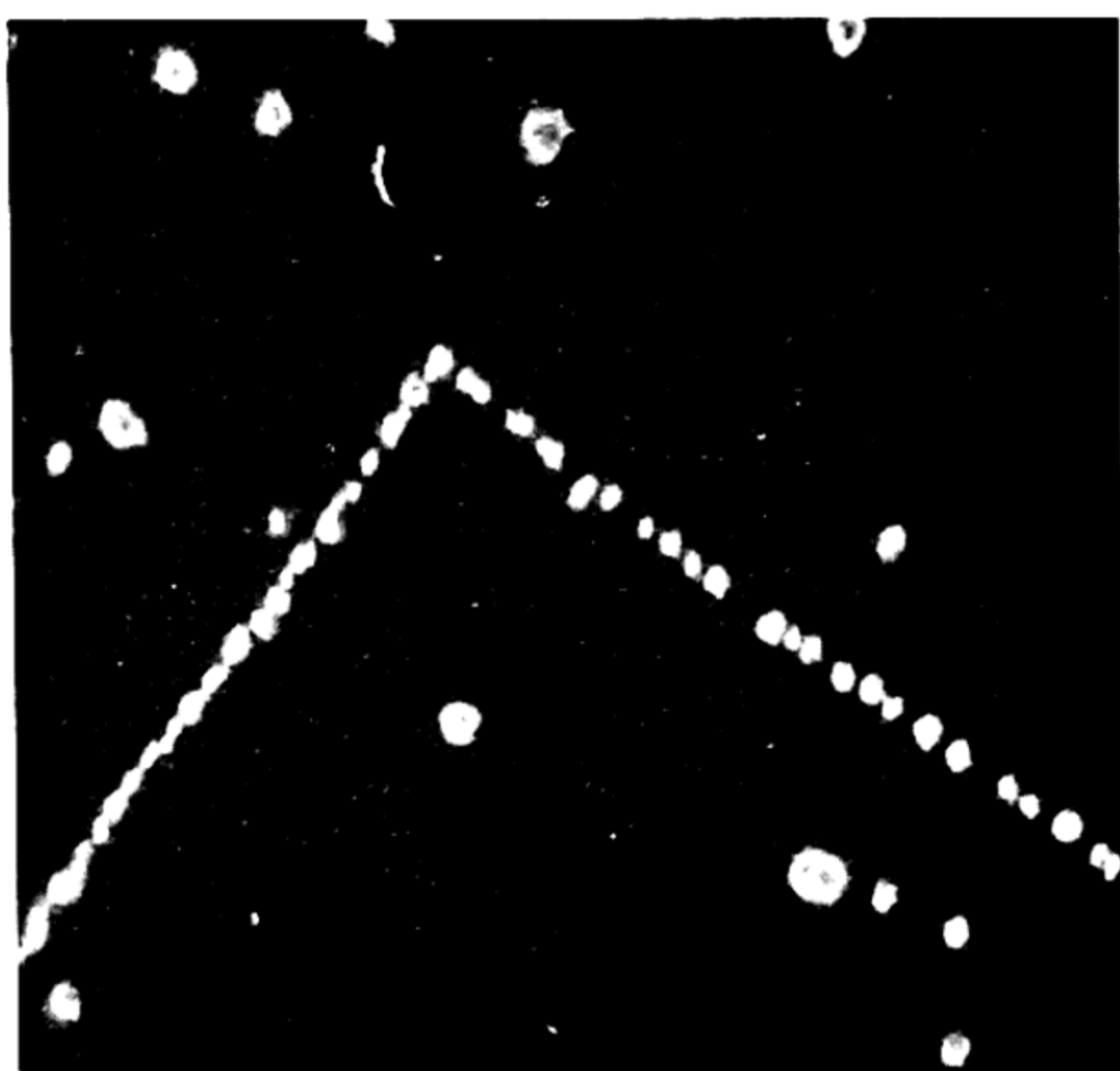


Figure 7. Particles in silver film on silica glass, heated to 230°C . ($\times 850$)

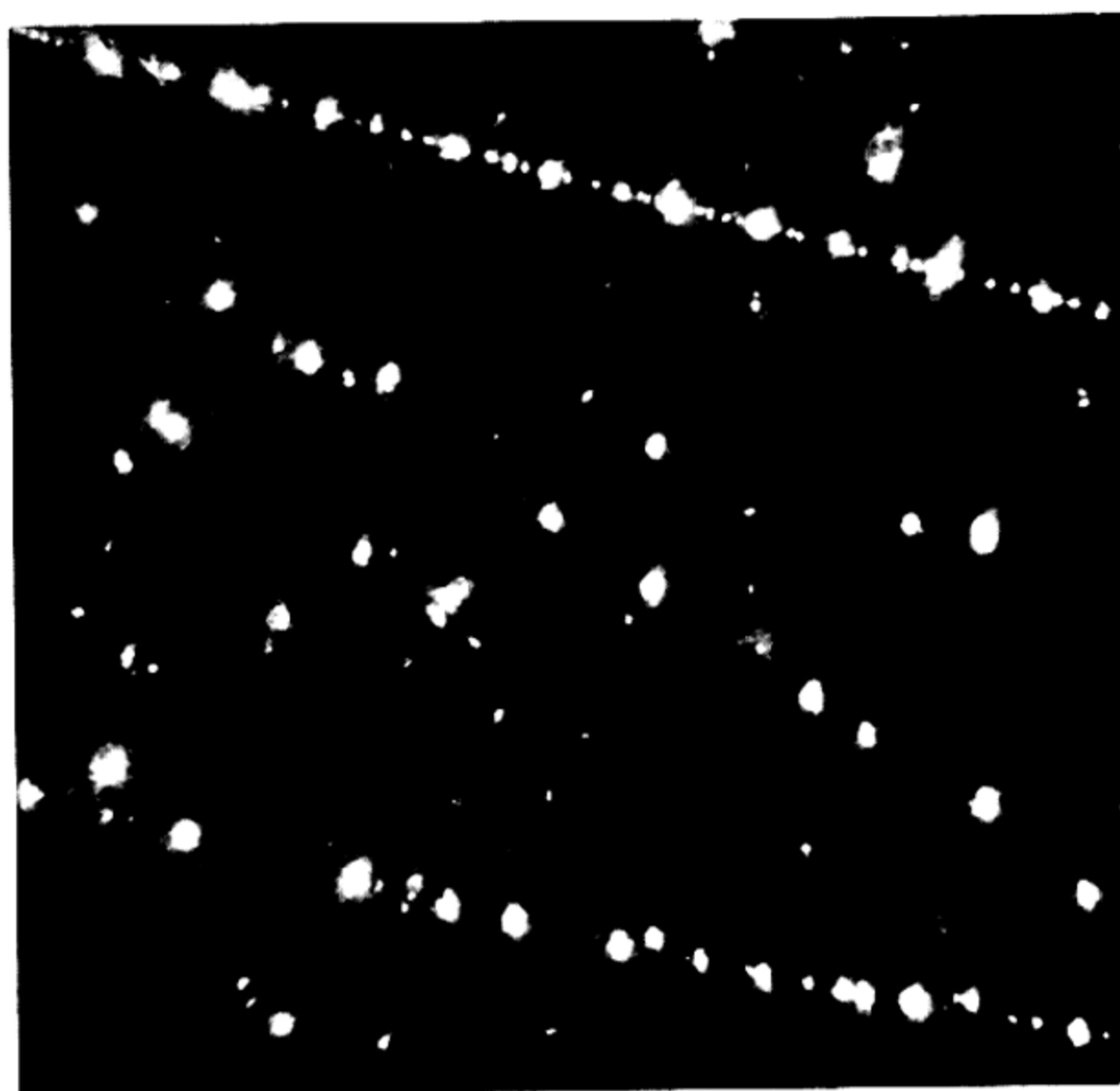


Figure 8. Particles on silica glass, under strong grazing illumination ($\times 850$)

the glass carefully cleaned and heated *in vacuo* (at 550°C . in the case of quartz glass), and a fresh film subsequently sputtered on it. This film, on heating, showed an identical pattern of lines, so that the effect survives very vigorous surface cleansing. On the other hand, abrasion and polishing of the surface, estimated to remove a layer 10^{-6} cm . thick, abolished the line formation. We concluded that the lines were due to ultramicroscopic surface cracks. Very strong grazing illumination failed to reveal any connecting line between the individual crystallites, as shown in figure 8, so that the cracks must be exceedingly fine.

To verify this, films were prepared on the natural surfaces of diamond crystals. Sir Robert Robertson, J. J. Fox and A. E. Martin* have shown that two types of diamond exist, for one of which (type 2) a mosaic structure is deduced from their experiments, while the other (type 1) is free from submicroscopic faults. Specimens of each type were lent to us by Prof. W. T. Gordon, and films prepared on natural (111) faces. The usual heating *in vacuo* was then carried out. In the case of type 1

* *Phil. Trans. Roy. Soc.* **232**, 463 (1934).

there was no tendency for the crystallites to form up in lines, as shown in figure 9* With type 2 very well marked lines were formed where no imperfection could be detected by the most rigorous conditions of illumination, as shown in figure 10.

The directions of these lines were measured. They could all be accounted for by

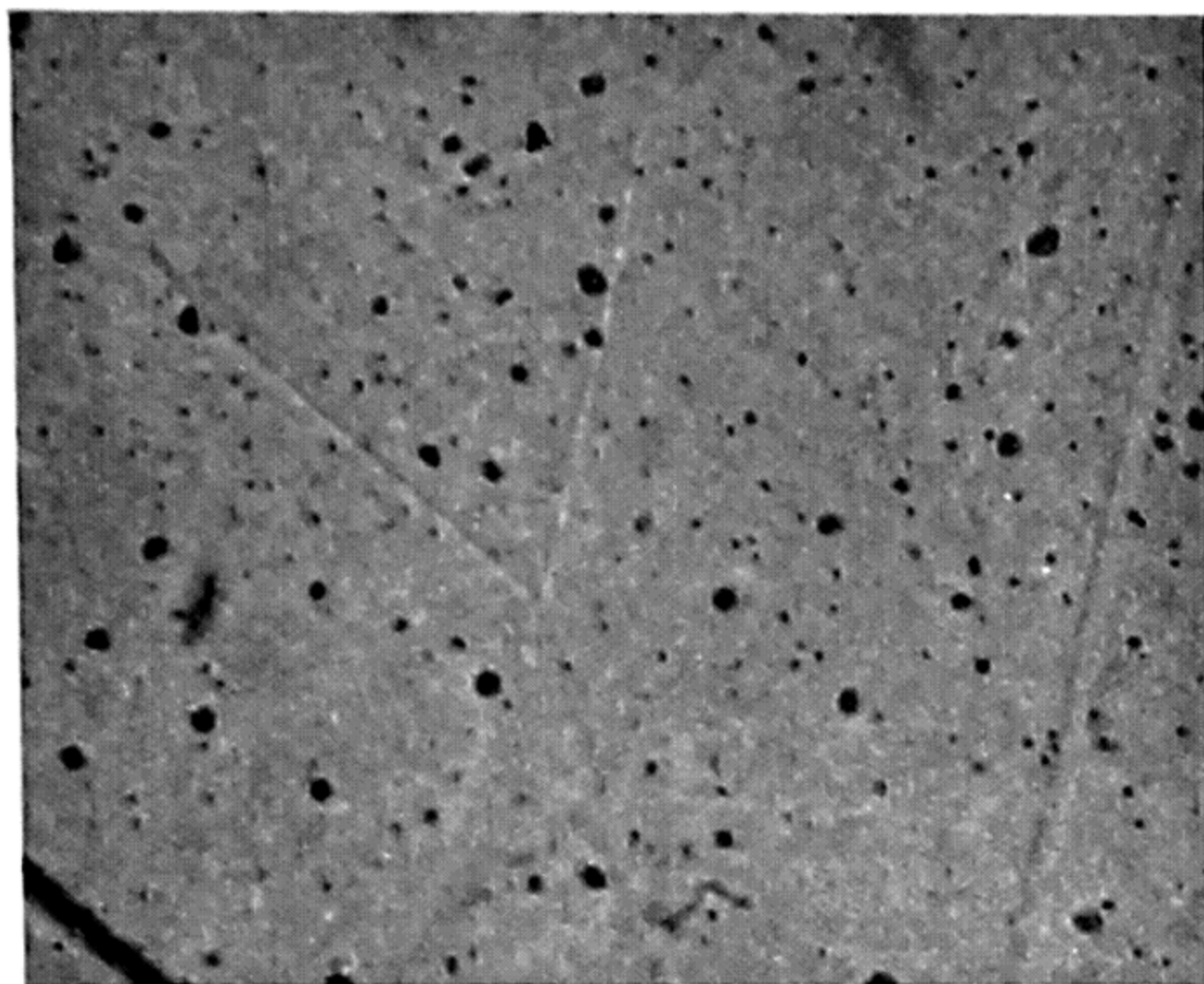


Figure 9. Particles on diamond, type 1 ($\times 850$)

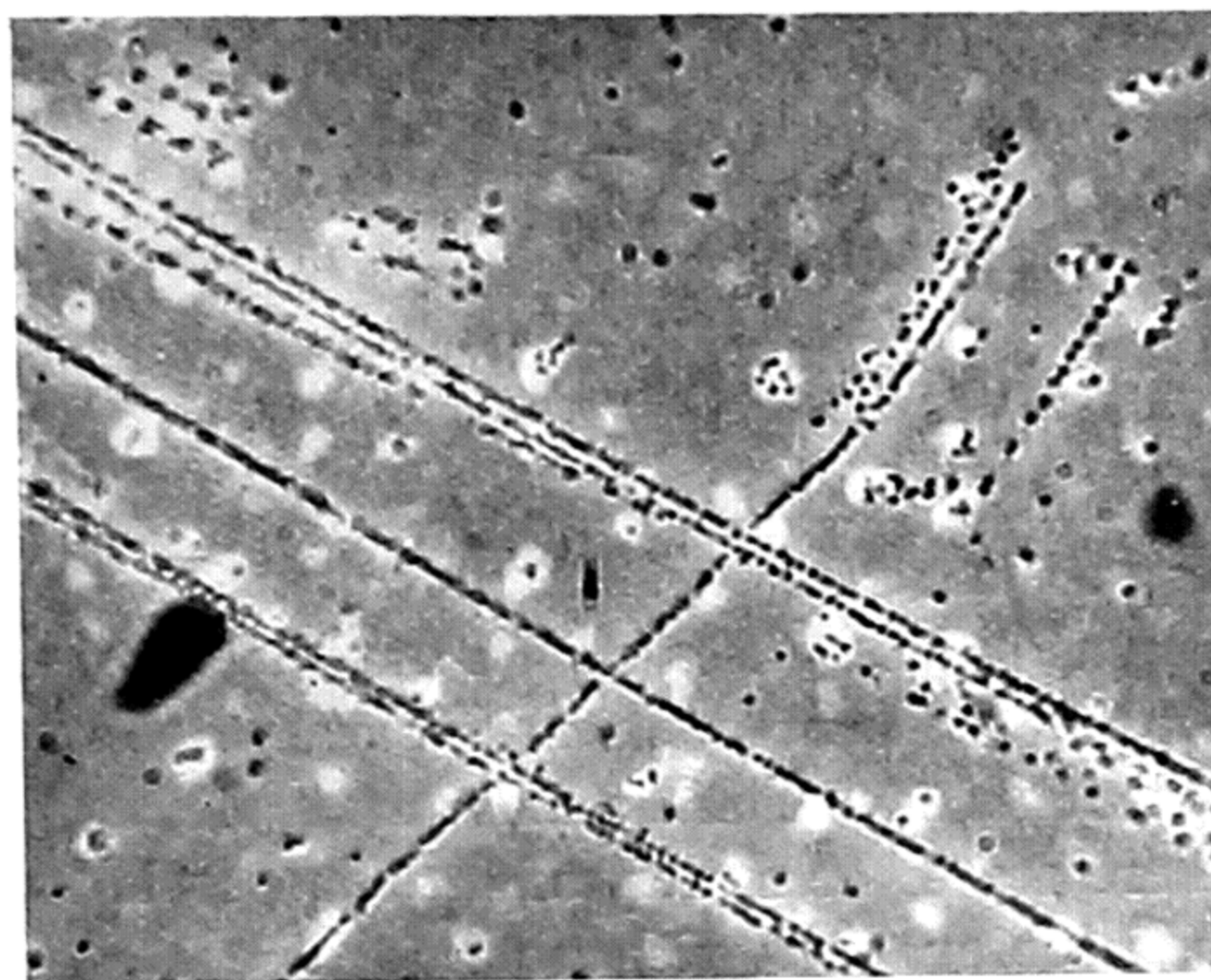


Figure 10. Particles on diamond, type 2 ($\times 850$)

intersections of planes, with no index higher than 2, with the (111) face, and one particular set of planes was strongly preferred.

There seems little doubt, then, that the formation of these lines of crystallites in metal films does really indicate surface flaws, too narrow to be detected by ultra-microscopic methods. If this is admitted it follows that these flaws have been directly shown to exist even in the surface of polished silica glass, as demanded by Griffith. The method seems promising, and is being further investigated by me in collabora-

* The triangle is the outline of a natural surface pit.

tion with Mr F. A. Walch. In particular, we intend to remove the polished surface and look for further flaws.

Referring finally to Prof. Goetz's observations on foreign atoms, the experiments with very pure mercury which I have quoted in the discussion on the final group of papers* tend to show that impurities play little part in the discontinuities in metal crystals, as evidenced by glide planes. In the first place there will, on these planes, be only one atom of impurity to every few hundred mercury atoms with our purest mercury, and in the second place the spacing of the glide planes is independent of impurity, which agrees with the findings of Prof. Goetz.

Sir WILLIAM BRAGG. It seems to be generally agreed that the "sensitive" properties are due to the existence of a condition which may be described as a series of faults, cracks or discontinuities of some sort. Zwicky has supposed that the discontinuities are regularly distributed in the crystal, being a consequence of the very nature and composition of the crystal. On the other hand, it is maintained that the discontinuities are distributed statistically, being a consequence of the mode of growth or other accidental circumstances. As to the origin of the discontinuities, no theory has been suggested, except that of Zwicky whose arguments in support of it seem to be unsound, and Buerger's interesting theory of lineages.

It may be worth while to consider the matter in the following way. The formula which is taken to represent the forces governing the assemblage of atoms in a crystal, viz.

$$\frac{e_1 e_2}{r^2} - \frac{A}{r^n}$$

is extremely simple. It cannot provide for all complications. A very natural way of making it more general would be to suppose that the repulsive force represented by the second term is somewhat directive. The effects of such anisotropy would only become evident when the temperature was sufficiently lowered. Thus in a crystal formed at high temperature the atoms would be arranged with geometrical regularity, and the compound would be free of strain. As the temperature falls, strain would enter: if the crystal were cold worked, its atoms would seek a slight readjustment. Let it be supposed that relief can be obtained without altering the general distribution of the atoms; there are to be merely slight changes in orientation and movements which are small in comparison with atomic spacings. This rearrangement will relieve the strain in various regions but will not be able to do so throughout the crystal without interruptions here and there where adjustments must be made involving definite discontinuities of the order of the distances that separate the atoms. Hence would arise the discontinuities of Griffith, Smekal, Joffé, Orowan, Taylor and others. One might compare the effect with that of packing together in close order bodies which were not quite spherical. The packing would proceed regularly for a time with a growing misfit, which would at last require a fresh start to be made.

In this way the crystal would become a mosaic. On occasion the blocks might possess some regularity in size and so account for the observations of Goetz and others.

* See p. 173.

A crystal formed from the melt would be geometrically regular in the first instance, but would, as the result of cold working, assume the mosaic form in which the blocks had in general lost their parallelism to some extent. This would provide the spacings (which he calls L) required by G. I. Taylor. Increase of cold working would increase the extent of readjustment and the prevalence of the mosaic structure, and with that the hardening. Annealing would have the contrary effect.

There is some support for such views in the fact that rock-salt crystals from the melt are geometrically more perfect (Ewald and Renninger) and yet have greater ionic conductivities and are more easily coloured by radiation: which would be expected if the separate atoms are not entirely at ease. And again in Robertson and Fox's two types of diamond, that which is the more perfect geometrically and has less of a mosaic character has more absorption bands than the other.

Again some such effect would account for the limitation in growth of certain crystals, and the persistence of association in companies of a definite order of magnitude that is found on melting.

Dr G. ANTONOFF. The notion of molecular weight has been established as a result of work with gaseous matter, and owing to the Avogadro hypothesis it has become possible to express the same in definite units. Thus, when matter is in a gaseous state, there is a rational method permitting us to determine the molecular weight of a substance experimentally.

But as soon as the material is presented in a state other than the gaseous, nothing definite is known about its molecular state, and the difficulty is in the want of methods for its determination. The substances in the liquid state are believed to be, according to the prevailing view, either "normal," if their molecular weight is said to be the same as in the gaseous state, or "associated" when the molecular weight is supposed to be a certain multiple of that in a gaseous state.

These views, however, are based on a number of empirical rules, whose theoretical foundation is very poor. Besides, their agreement with facts is also highly illusory.

As regards the solid state, practically nothing definite can be said about it. It is even not obvious whether the question of molecular weight in the solid state can arise at all. The X-ray method does not answer the question.

Under such circumstances, it is nowadays realized by some authors that the problem must be solved on quite a different basis, and that some general principle is necessary, a principle analogous to that of the Avogadro hypothesis, which would give a rational solution of the problem for states other than the gaseous.

Assuming with van der Waals the existence of molecular forces, I have deduced some relations which connect the number of molecules per unit volume with other properties of matter.

Imagine a crystal of rectangular form, which consists of molecules at an equal distance from one another. This is represented by dots in figure 1 where each dot represents a molecule. Each molecule is supposed to originate a uniform field of force, no matter what is its nature, which may be different in various cases*.

* J. E. Lennard-Jones, *Proc. Phys. Soc.* 43, 461 (1931).

This hypothesis is not the only one possible, but the result obtained remains substantially the same, and independent of the actual form of the law of attraction. For this reason, I limit this investigation to one form only.

Imagine a line AB in the surface, connecting one row of molecules of unit length. The adjacent rows of molecules will exercise a pull on the line AB . Consider at first only the forces acting in the surface $MNPG$ tangentially to it. The effect of molecules situated on one side of the line AB , summed up together, results in a force OC , which is generally called the surface tension.

It can be shown in a similar way that owing to the presence of molecules situated below the surface $MNPG$, there will be also a pull exercised on line AB in the direction perpendicular to OC and acting inwards, represented in the drawing by line OD . It will be of the same order of magnitude as OC assuming that the field of force is symmetrical, and will be somewhat bigger, as molecules on either side of the

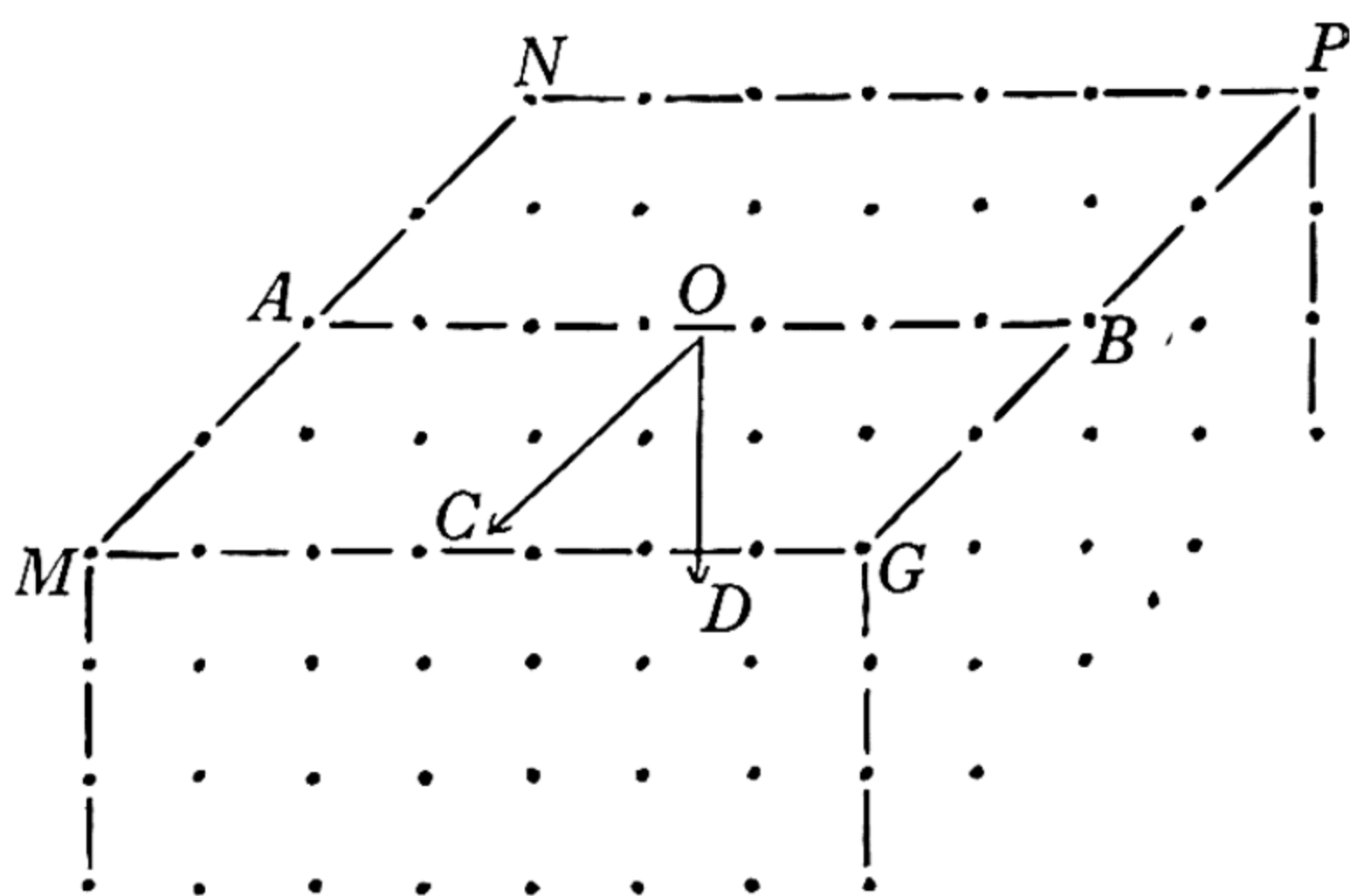


Figure 1

line AB will act jointly in this case. The field of force, according to the prevailing theories, is of such a nature that the force varies inversely as a high power of the distance.

Consequently in the summing up of the forces due to individual molecules, the adjacent row of molecules will contribute the most important term in the sum. The total force acting on the whole surface $MNPG$ inwards will be obtained by summation of forces acting on all rows in the surface. This inward force per unit area of the surface is generally called molecular, or normal, pressure.

It thus appears that if the number of molecules and their distance from one another is known, one can easily derive the normal pressure from the breaking stress of the crystal, and thereby also calculate the surface tension.

However, in practice, it is not possible to proceed in this way, as one gets ridiculously low figures from the breaking experiments*, incompatible with other evidence. This is generally attributed to the fact that the crystal is never perfect and always has small invisible cracks, which diminish the resistance to traction to a considerable extent.

* Antonoff, *Phil. Mag.* **44**, 63 (1922); *Z. f. Phys. Chem.* **102**, 388 (1922).

I shall therefore reverse the problem and calculate the inward pressure from the surface tension, which I can measure experimentally by a special method, which is independent of all imperfection in crystalline structure, and which I shall describe later on.

For my calculations I shall use the formula

$$P = K\alpha n^{\frac{1}{3}},$$

where P is the normal pressure, K is a constant, α is the surface tension, and n the number of molecules per unit volume*.

In some previous publications this formula was used by myself for calculations assuming $K=2$ (*Phil. Mag.* **38**, 419 (1919); *ibid.* **44**, 63 (1922); *Z. f. Phys. Chem.* **102**, 389 (1922)). In the case of rock-salt, K may be put equal to 1.

As regards P its value derived from breaking stress experiments is generally ridiculously low. Putting the experimental value into the formula, I found for the surface tension of rock-salt the value 1.4 dynes per cm. Such a low value may mean either that the value of P is so low owing to some imperfection in crystalline structure, or our notion of molecular state is not correct.

As a matter of fact, the data available in the literature (Ostwald, *Z. f. Phys. Chem.* **34**, 503 (1900); Hulett, *ibid.* **37**, 385 (1901)) suggested such values for the surface tension of solids as 4000 dynes per cm.

Assuming the attractions to be purely electrical, I obtained the value 3500 dynes per cm. (*loc. cit.*).

Under such circumstances, I made it a point to devise a method for determination of surface tension of solids, which does not involve the knowledge of n , the number of molecules per unit volume, and which would not depend on any imperfection in structure.

This I did in the following way (*Phil. Mag.* **1**, 1258 (1926); *ibid.* **4**, 792 (1927)).

I prepared pastes by mixing certain pigments such as lampblack, with inoxidizable oils. I determined the surface tension of these pastes of various concentrations from the breaking stress of their films. With increased concentrations of the pigment, the surface tensions of the pastes increase enormously, and may reach such values as 1000 dynes per cm.

I take advantage of the fact that these pastes wet the solids when their surface tension is small. If one takes pastes with greater surface tension, a point may be reached where the paste ceases to adhere to the solid. At this stage the surface tension of the paste is equal to that of the solid.

This method was checked by a number of experiments with bodies having a low melting point, whose surface tension could be determined by the capillary method in the liquid state. Knowing the temperature coefficient one could see that the method described gives correct results. Thus, I found for the surface tension of rock-salt the figure 315 dynes per cm.

By substituting this figure into the formula

$$P = \alpha n^{\frac{1}{3}},$$

* This formula was deduced in another publication, see *J. Phys. Chem.* (Sept. 1932).

I calculate P , assuming

$$n = \delta/M = 2.15/1.64 \times 58.5 \times 10^{-24},$$

where $\delta = 2.15$ is the density of rock-salt, and M its molecular weight. I thus obtain:

$$P = 88.5 \text{ kg./mm}^2,$$

which according to this theory is the highest possible value. The experimental figures, except those obtained by Joffé for rock-salt in hot water, are much lower as a rule. I attribute this to the cementing effect of water.

However, the experimental data are very divergent in the hands of different authors. The figures of Smekal and his school do not agree at all with those of Joffé and others, so it is very difficult to draw any definite conclusions at all from the breaking stress experiments.

Taking my own results, there is a considerable difference between the calculated value for the surface tension of rock-salt from purely electrical data, viz. 3500 dynes per cm. and the figure obtained experimentally—315 dynes per cm., of which I am quite sure. The discrepancy between them may mean that weakening of the system is due to the fact that 11 molecules or so combine in some way to a grouping, which in some experiments may behave as a separate unit. If this is so, the normal value for the breaking stress would be about 39 kg./mm².

This is one possibility I can think of in favour of the theory of a secondary structure.

Another theory can be deduced from the laws of equilibrium between different phases of the same substance, i.e. liquid, vapour and solid.

Willard Gibbs found that two liquid phases in equilibrium (i.e. two superposed partially miscible liquids) have the same vapour pressure. This can be also proved experimentally.

Let us call p the vapour pressure. Then

$$p_1 = p_2 \quad \text{.....(1),}$$

where p_1 is the vapour pressure of one layer and p_2 that of the other, may be described as one of the conditions of equilibrium.

I found experimentally in 1907 that in a state of equilibrium the following law can be stated to be true:

$$\alpha_{12} = \alpha_1 - \alpha_2 \quad \text{.....(2),}$$

where α_{12} is the interfacial tension, α_1 and α_2 the surface tensions of two saturated layers against their common vapour. I generally call it a "law of difference."

I can also deduce it theoretically. This can be done subject to the condition

$$n_1 = n_2 \quad \text{.....(3),}$$

where n_1 is the number of molecules in the one layer and n_2 in the other.

This relation can be stated to be the third condition of equilibrium.

These conditions (1), (2) and (3) are so correlated that if one of them can be proved experimentally, it automatically involves the others.

The fact that the experimental evidence indicates a full agreement between them, appears to be a proof that the ideal gas laws hold true in such cases. From the fact

that the molecular concentration is the same, both layers must have the same vapour pressure according to Raoult's law. Both layers also have the same freezing point, separating the same ice, and they boil at the same temperature. In other words they are identical in all those properties which depend upon the number of molecules and not their nature.

In an extensive paper (*loc. cit.*) I gave the whole theory, where the above conditions were shown to hold true also for other interfaces.

Thus, I show that liquid and vapour in equilibrium contain an equal number of molecules per unit volume.

At the melting point, when the solid, liquid and vapour are in equilibrium with one another, the same theory must apply.

Thus, the degree of association of the solid at the melting point must be represented by the ratio

$$x = \delta_s / \delta_v,$$

where x is the factor of association, δ_s density of the solid and δ_v that of vapour.

The molecular weight will be found by multiplying the molecular weight of the gaseous phase by x .

The theory set out points to the existence of a secondary structure in one sense. In the mobile equilibrium between the phases, the particles of the solid must detach themselves in groupings of a considerable degree of complexity. Such units may comprise hundreds of thousands of gaseous molecules, according to the evidence in existence. However, if this character manifests itself in kinetic properties, it does not necessarily mean that it will be revealed by all other properties.

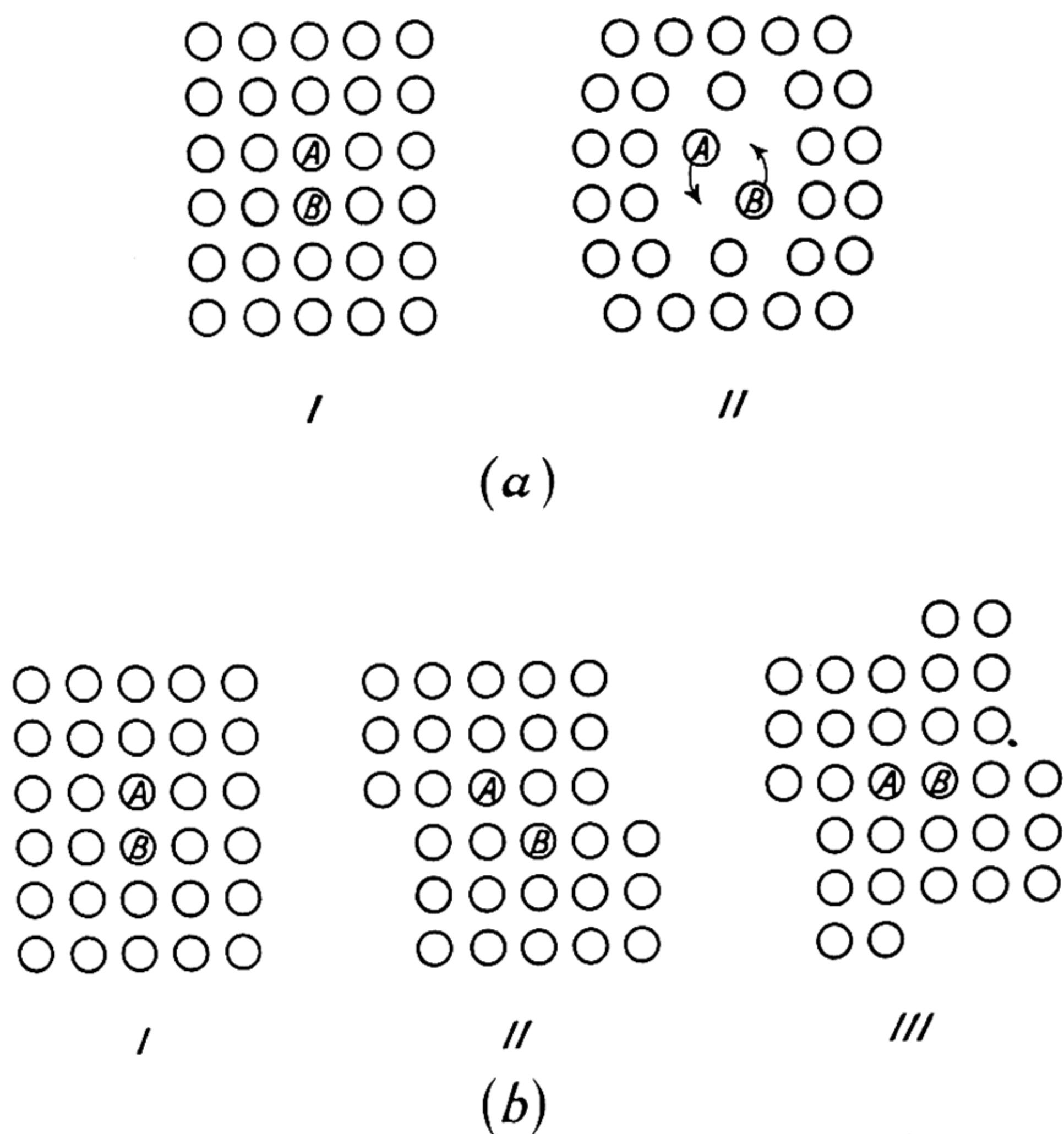
Dr J. D. BERNAL. I should like to draw attention to an aspect of the crystalline state that is not usually considered, namely the fact that at room temperatures most crystals which have been studied, e.g. metals, salts, etc., are not in internal thermodynamic equilibrium.

I have been led to this point of view by considering the relations between liquids, glasses and crystals. A liquid and its glass, in case it forms one, have at any moment the same molecular structure, but a glass, from the very fact that it can be strained and can have different properties according to the heat treatment it receives, is not in internal thermodynamic equilibrium. A super-cooled liquid *per se* is no different from a true liquid. The fact that a crystalline array may have lower free energy at the temperature concerned does not remove the internal stability of the liquid, and there is no discontinuity in its properties at the melting point. There is, on the contrary, a definite change in properties over a range of temperature well below this. Some properties such as viscosity change by enormous factors; others, such as density, hardly change at all. Now there is no reason to suppose that just because in a crystal the arrangement of atoms is regular, similar phenomena will not take place at a temperature below the melting point. A normal crystalline solid may be crystalline in structure but thermodynamically vitreous, able to exist in states of different free energy at the same temperature. The change need not be abrupt, in fact it may be less so than in glasses, but it has already been recognized in the

existence of the recrystallization temperature range above which permanent strain is impossible.

The elementary mechanical theory of crystals strictly only applies when they are in thermodynamical equilibrium, and for processes the time scale of which is comparable with the rate of reaching equilibrium. Incidentally, no theory of crystalline plasticity can be really satisfactory that does not introduce explicitly the idea of a characteristic time.

The high plasticity of crystals above the temperature of recrystallization suggests strongly that they have no true rigidity. If we neglect surface forces, a glide along a



crystal plane leaves the internal energy unaltered, and requires, therefore, no work but only an activation energy. Now, just as in the corresponding case of electrical conductivity, we must imagine external forces merely to superpose their effect on the spontaneous gliding that takes place without external forces. We have in any case to assume this gliding to account for true crystalline diffusion (apart from diffusion along cracks). It is usually assumed without much thought that in diffusion, atoms change their places, neighbouring atoms simply moving out to let them pass, and then closing in again, as in the upper part of the figure. The activation energy of such a process is much too great to occur in a crystalline solid. The amount of disorganization required is only compatible with the liquid state.

It is much more probable that diffusion takes place by repeated spontaneous

gliding along different planes, as shown in the lower part of the figure. Such spontaneous gliding gradually diminishes with temperature, as does the diffusion, until below a certain temperature both are imperceptible. The forced gliding that occurs at lower temperature when the crystal is internally "glassy" must be of a different nature. I think that for this Prof. G. I. Taylor's mechanism, or some variant of it, is the most plausible. As it stands, however, it contains a paradox. The fewer the dislocations the weaker the crystal, but a crystal with no dislocations would be infinitely strong. However that may be, the dislocations probably exist at high temperatures as fugitive singularities which are "frozen" in at low temperatures, more or less appearing according to the rate of annealing. Once there, they cannot disappear and can only be made to move by external strain.

Dr J. BRENTANO. The fact that the mosaic structure is not a constitutional property of rock-salt, which results from Prof. Ewald's measurements on large crystals, is also found for smaller crystals obtained by distillation. I prepared crystals of about 10^{-3} cm. side by the slow distillation of chemically pure sodium chloride in a vacuum and found that the intensities of their X-ray reflections corresponded within 10 per cent with the intensities expected from perfect crystals. Mechanical grinding increased the intensities of reflection and brought the crystals into an intermediate state between perfect crystals and mosaics. The comparison of the intensities after grinding, with those from powders of chemically precipitated sodium chloride, sufficiently fine to give no appreciable extinction, showed however that the process of mechanical grinding is inadequate to break up completely the regular lattice of the crystals originally obtained by distillation.

Dr W. G. BURGERS. The following considerations (compare A. E. van Arkel and W. G. Burgers, *Polytechn. Weekblad*, **28**, 547 (1934)), although not applying directly to the lattice-deviations considered in Prof. Smekal's paper, may perhaps be of interest in connexion with the question whether there exists any correlation between a *definite* structure-sensitive property and the "character" of the "lattice-irregularities" by which it can be influenced. For metals and alloys this seems to be true at least to some extent, as can be deduced from a study of the sharpness and intensity of their Debye-Scherrer interference lines. So, for example, the well-known fact that the electric resistance of an alloy, giving sharp Debye-Scherrer lines, is in general much higher than that of the pure components, shows that this property is influenced by "lattice-irregularities" of the order of the atomic distances, thus being of extremely small "period." On the other hand, the stresses required for an increase in coercive force, probably require regions of "homogeneity" of the order of magnitude of 0.5μ , as seems to follow from the fact (see for example W. A. Wood, *Phil. Mag.* **13**, 355 (1932)) that in this case a broadening of the Debye-Scherrer lines is often observed. Hardening, again, may perhaps be connected with irregularities of smaller period. In fact, strongly cold-worked aluminium, although exhibiting a considerable hardening, shows no appreciable broadening of the Debye-Scherrer lines (see U. Dehlinger, *Z. f. Krist.* **65**, 615 (1927)), whereas cold-worked tantalum, while exhibiting a pronounced broadening

of these lines, shows neither marked hardening effects, nor a pronounced increase in electrical resistance (W. G. Burgers and J. C. M. Basart, *Z. f. anorg. Chem.* **216**, 223 (1934)). Similar conclusions can be drawn from papers by G. Kurdjumow and G. Sachs on the hardening of carbon-steel (*Z. f. Phys.* **64**, 325 (1930)) and by J. Hengstenberg and G. Wassermann (*Z. f. Metallk.* **23**, 114 (1931)) on age-hardening of duralumin. Especially during ageing of definite alloys it is well known (for example W. Köster, *Stahl u. Eisen*, **53**, 849 (1933)) that the various physical properties considered above often do not vary simultaneously, which fact again points to the possibility that they are influenced by lattice-irregularities of different "periods."

M. F. CANAC. The so-called plane surface of a solid consists in reality of an assemblage of elementary crystal faces each with an area of several square microns, forming polyhedral "holes" or "humps." The light scattered from the surface is due to reflection on these minute faces. The distribution in space depends on the number and the size of those faces which are in a position to return the light in a given direction. If the corresponding relations are determined, simple photometric measurements suffice to give the "mean topography" of the solid.

If the facets are all parallel, the surface is perfectly polished. If they are distributed equally in all directions, the holes or humps will on the average be spherical. We are thus led to study reflection from a plane covered with little reflecting spheres, or dotted with reflecting hemispherical holes. It is found by calculation and verified by experiment that such a plane scatters light with the same intensity in all directions, subject to the obvious condition that the rays are not stopped by the edges of the holes or by the surfaces of the spheres. The deviations from this law depend on the extent to which the individual holes deviate from the mean.

If the surface is formed by hollows which are approximately hemispherical but which have on their surfaces other smaller holes or humps of the type mentioned above, then the light scattered in a given direction is of the form $(A - Bi)$, where i is the angle of incidence of the beam.

If the surface has deep cracks with walls which diffuse as in the previous cases, the scattering is of the form $(A - B \tan i)$.

By illuminating surfaces at various angles, and measuring the distribution of scattered light, I have traced the scattering indicatrix for the different surfaces. The predictions are more nearly verified, the closer the holes approach to their mean.

In this way I have been able to verify them in a precise manner on many specimens of alloys. In this way each of the three types of surface mentioned above has been found to exist, the type with deep cracks occurring particularly for intercrystalline corrosion. The method allows us to follow the process of corrosion, to discover the form of the resistant parts of the solid, and to form an idea of their structure.

Finally, it may be mentioned that when the faces have a preferred direction (lamination), this also can be brought out clearly by the method.

Dr J. A. DARBYSHIRE. I was interested in the little spherulites which Prof. Andrade described as existing in the thin films of sputtered gold and silver. During

the course of some experiments on electron diffraction we were passing a beam of high speed electrons (30–36 kV.) in a normal direction through thin films of cadmium oxide in which there were small crystals of metallic cadmium suspended in some way in the oxide film. We obtained well defined spot patterns which we tried to interpret as two-dimensional cross-grating effects in a manner similar to the interpretation usually given to the cross-grating patterns formed when a beam of electrons passes through very thin mica. We found many difficulties in such an explanation and it appears more likely that the effects are due to aggregates of little crystallites somewhat similar to the spherulites of Andrade but with a great many of the side chains stripped off, leaving a cone of chains about the direction of the beam as axis, that is, normal to the plane of the film.

Prof. G. I. FINCH. The study of surfaces by the method of electron diffraction has brought to light the fact that the normal crystal structure of a surface film can be profoundly modified by the nature of the substratum upon which the film has been formed. For example, G. P. Thomson⁽¹⁾ found that the orientation of the crystals of a silver film was that of the silver substratum upon which they had been formed by electro-deposition. My collaborators and I have also observed a similar effect in the case of platinum films formed by cathodic sputtering on to a crystalline platinum substratum. An even more remarkable demonstration of how eagerly even a foreign atom may enter into the building up of an ordered crystal structure is afforded by the phenomenon of basal-plane pseudo-morphism⁽²⁾ as shown, for example, by aluminium (normally face-centred cubic, $a = 4.05 \text{ \AA}$.) which when deposited in a thin layer on platinum (face-centred cubic, $a = 3.91 \text{ \AA}$.) acquires a face-centred tetragonal structure, $a = 3.91 \text{ \AA}$., $c/a = 1.03$; thus in this case the platinum substratum imposed its basal crystal dimensions on the aluminium without, however, affecting the normal spacing of the aluminium lattice in the direction of the c axis. Phenomena such as these testify clearly to the urge impelling newly arriving atoms to continue extending a structure rather than to start building a new one; and if the block structure in crystals is sub-microscopic then the underlying cause of such discontinuity must indeed be powerful. Prof. Lennard-Jones has just suggested that lattice contraction due to electrostatic forces in small ionic crystals might produce the effect. Quite recently Dr Wilman and I⁽³⁾ have redetermined by electron diffraction the lattice dimensions of zinc oxide using gold as a standard for reference. Whilst our value for c/a agrees excellently with W. L. Bragg's for zincite⁽⁴⁾, our a and c values are about 1 per cent higher than his. Now, the crystals we examined were exceedingly small, probably appreciably less than 100 \AA . in length; further, the binding forces in zinc oxide crystals are probably mainly atomic and not electrostatic, and in such a case, according to Lennard-Jones' theory, the lattice dimensions should increase with decreasing crystal size. Thus Lennard-Jones' theory appears to afford a reasonable explanation of the high values found by us for the zinc oxide lattice constants.

We are continuing our experiments with a view to determining the effect, if any,

of crystal size upon the lattice dimensions of ionic crystals, and the results so far to hand do seem to support Lennard-Jones' theory.

REFERENCES

- (1) G. P. THOMSON. *Proc. R. S. A*, 1 (1931).
- (2) FINCH and QUARRELL. *Proc. R. S. A*, 141, 398 (1933).
- (3) *J. Chem. Soc.* 751 (1934).
- (4) *Phil. Mag.* 39, 647 (1920).

Prof. R. H. FOWLER. I should like to comment on Dr Goetz's very beautiful experiments on the effects of small amounts of impurities, with their critical upper limits. I do not think that the experiments should be assumed to throw any light on secondary or group structure, or to indicate that the foreign atoms congregate at low concentrations on to intercrystalline planes or faces, until they have been carefully examined in the light of the recent work of Dr H. Jones on the importance of the Brillouin zones in this connexion*. I am especially suspicious of Dr Goetz's interpretation, because of his remark that metallic impurities of valency ($V-1$) and ($V+1$) affect a metal of valency V in opposite directions. Dr Jones has already had marked success in explaining many of the properties of bismuth itself by applying just the ideas to which I want to call attention. Briefly his fundamental idea is that many properties of metallic alloys are largely determined by the adjustment of the number of valency electrons of the atoms in the unit cell of the lattice to the possible number of states inside the first (or first set of) Brillouin zone, when that zone or set of zones is separated from the next by a strong energy discontinuity. On this view, the foreign atoms replace the regular atoms at ordinary lattice points and the opposite behaviour of impurities of valency ($V-1$) and ($V+1$) is at once understood. Dr Jones has given reasons why these changes of free electron number per cell should have some at least of the large effects observed. The critical concentration found by Goetz might well indicate, on this point of view, the complete filling or emptying of some zone. I am not, however, in a position to do more than call attention to this work and the need for correlating it with these experiments.

Sir R. HADFIELD. With regard to the two papers by Joffé, it would appear that the general conclusions arrived at prove that in embrittled materials the tensile strength is to some extent determined by surface imperfections (crevices). The author infers that these imperfections are spread throughout the material. It would be interesting to know whether Dr Joffé would apply this theory to the greater strength of thin steel or iron wires, as compared with thick ones. At the commencement of his paper "On the Mechanism of Brittle Rupture" he appears to be referring to steel wires. If so, his conclusions are important and we must look to small particles of carbide or possibly even what he calls inclusions to explain by their appearance on the surface of the wire the lower strength of thick wires as compared with thinner ones. At the same time, it would be difficult to get away from existing ideas that the

* The structure of alloys in the γ -phase, *Proc. R. S. A*, 144, 225 (1934) and other papers in course of publication.

greater strength is due to the greater amount of work hardening produced in drawing.

We have already a certain amount of evidence that defective surface reduces the tensile strength of brittle materials. To get the highest tensile strength from a fully hardened steel it is necessary to give the surface a high polish. That is really equivalent to removing surface irregularities and not quite the same thing as that to which the author is referring, except in so far as the process removes scratches.

It may be of course that when we have done our best in this way, that is by polishing, we still do not get the true tenacity. In fact we know this to be the case. There may therefore be something in the author's idea that the "outcropping" on the surface of small particles or whatever they may be, spread through the mass of the steel, also has an important effect on the strength.

Attention was called to this question of the difficulty of getting the true tenacity of brittle materials both in the paper by Prof. W. J. de Haas and myself* and also in my paper on "Alloys of Iron and Manganese containing Low Carbon" read before the Iron and Steel Institute in 1927.

The commencement of the paper by Joffé "On the Cause of the Low Value of Mechanical Strength" goes somewhat in the direction of trying to connect tensile strength with molecular cohesion, and to this extent is most welcome, especially in view of the plea put forward for attention by physicists to such questions in the conclusion to the paper by Prof. W. J. de Haas and myself referred to above.

The detection of an elastic limit by X-ray methods is very interesting, as also the statement at the beginning of §3 which says "if the elastic limit increased by... lowering of temperature reaches the value of the practical tensile strength the material becomes brittle." Are we to understand that this explains the general embrittlement of iron and most ferrous alloys as well as a material like quartz? If so, why does it not happen with nickel or with the alloys of iron containing fairly high percentages of this metal?

Paragraph 9 of this paper "On the Cause of the Low Value of Mechanical Strength" is of great interest because here the author is discussing the question of what we call work hardening, or as he calls it increase of tensile strength with plastic deformation. The author explains that this is only a secondary effect, and says why; but it would be interesting to know how it can occur to such a marked degree in manganese steel and even in nickel on the one hand, and only to a comparatively slight degree in iron. It will be noted also that the author mentions that amorphous, i.e. non-crystalline, bodies show none of this work hardening effect.

With regard not only to the two papers by Joffé but also to that by Dr E. Orowan I should like to know what the authors consider occurs in the case of forged and water-quenched manganese steel in which there is exceedingly low elastic limit, in fact as low as 8 to 10 tons per square inch and probably still lower. The "strains" produced, whilst exceedingly minute, are nevertheless present.

The theory put forward by Dr Orowan connecting the reduced tensile strength of materials with that calculated from considerations of atomic cohesion is certainly

* *Phil. Trans. Roy. Soc. A*, 232 (1933).

a useful contribution and adds force to the observations of Joffé in so far as it shows that the breakdown of crystalline materials can occur as the result of quite minute surface defects.

Apparently, however, the theory as described only applies to single crystals. In multigranular metals like iron and its alloys as we find them in practice, the breakdown first occurs in crystal grains in which the slip planes are favourably directed in relation to the stretching force. For breakdown to occur from a surface defect it would appear necessary therefore that the defect should occur inside one of these particular crystals.

In Dr Orowan's paper, page 83, considerations seem to be based on Hooke's law but this appears to have a very limited range of validity in single crystals, in which the elastic or proportional limit is very low indeed.

Dr A. JOFFÉ. The important contribution of Sir Robert Hadfield raises the problem of applying results and considerations drawn from the study of single crystals and glasses, to a multicrystalline metal.

Now there is a fundamental distinction between brittle glass fibres on the one hand, and cold-worked and drawn metal wires on the other, these at room temperature and the usual rates of loading being in a plastic state. The influence of the thickness is partly explained by the hard-worked layer of a metal wire. Nevertheless I should think that sharp inclusions are responsible to a considerable degree for the actual strength of a wire.

Again, both steel and quartz become brittle at the crossing point of the curve for the yield point and that for the strength. (The X-ray method gives the value of the yield point and not of the elastic limit, which is very low for single crystals.) It seems that the yield point of nickel and nickel alloys does not increase, or only increases slowly, when the temperature decreases. Unlike the case of carbon steel, there may not be a crossing point at attainable temperatures.

Finally, the marked difference between manganese steel and iron may be due to the phase changes taking place during the cold working of manganese. Austenite is often transformed into martensite with accompanying change of magnetic properties. Moreover, the low elastic limit of quenched manganese steel is less important for the rupture than the yield point, which seems to lie higher.

Dr E. OROWAN. 1. I am very glad that a remark of Sir Robert Hadfield gives me an opportunity to call attention to the fact that the plastic crack-propagation mechanism is also applicable to internal cracks. In my paper, I considered surface cracks only, because of their practical importance; we know, indeed, from experience that rupture starts actually in most cases from a surface crack. It is, however, easy to see that an internal crack can be propagated in exactly the same way as a surface crack, if a set of slip-planes near its edge comes into action. At the same time, the stress at the opposite part of the edge increases, because of the widening of the crack; thus a plastic propagation of an internal crack can also lead to a rupture by a notch-effect.

2. Both the notch-effect mechanism of Griffith and the plastic mechanism of

crack-propagation, apply directly to a single crystal or to a single grain of a polycrystalline body only. For the rupture of multigranular bodies, such as technical metals, a second criterion must also be fulfilled: namely, the crack, after having spread across an unfavourably directed or located grain, must penetrate into the adjacent grains. Because of the different lattice orientation of different grains, the passage of a crack beyond a grain boundary generally needs a stress which is considerably higher than that necessary for propagation within a single uniform grain. This is the cause of the high strength of multigranular bodies as compared with single crystals*.

3. As to the very limited range of validity of Hooke's law in single crystals, this is caused exclusively by intervening plasticity phenomena which are not essentially connected with the elastic strain; so their occurrence does not imply a failure of Hooke's law, just as the burning out of an incandescent lamp on reaching a certain voltage does not signify that the law of Stefan and Boltzmann becomes invalid beyond this critical temperature. Thus the use of Hooke's law for calculating the order of magnitude of the theoretical strength, as suggested by Professor Polanyi, must be considered as correct.

Dr B. LOCKSPEISER. I should like to ask Sir William Bragg whether the model put forward by him involves surfaces of discontinuity within the crystal, dividing parts of the crystal of different energy contents from each other.

Sir W. BRAGG. It would be a probable consequence of my suggestion that a mosaic crystal and an ideal crystal would have different energy contents. So far as I know, however, heat of dissolution has never been found to be a "sensitive property." But the degree of sensitivity might be small, because the changes in position and orientation, which I have assumed tentatively, are small and the energy change which they involve might be small also, even though the forces were large. Thus the regions on two sides of a discontinuity might have different energy contents if they differed in mosaic character.

Dr E. OROWAN. In his Opening Survey, Sir William Bragg pointed out that a difficult problem of the crack-propagation theory of tensile strength is given by the question, how from the action of accidental cracks a more or less sharply defined strength can result. That accidental cracks can produce a sharply defined strength at all, has been proved in the case of mica. The ordinary tensile strength of mica lamellae is determined by cracks on its edge (see E. Orowan, *Z. f. Phys.* 82, 235 (1933)). Now lamellae with a ground edge show a tensile strength which can be reproduced within a few per cent (*loc. cit.* p. 249 and figure 6) and so belongs to the most sharply defined tensile strengths known. Thus the question, how accidental cracks can give a definite tensile strength, is, of course, a difficult problem, but no difficulty for the crack-propagation theory.

The explanation of this problem given by Prof. Joffé in his paper "On the Mechanism of Brittle Rupture" is strongly supported by the fact that the strength of mica lamellae with a ground edge is much more sharply defined than that of

* Cf. E. Orowan, *Z. f. Phys.* 86, 200 (1933).

lamellae which have been cut with scissors. Since the number of cracks is much greater in the first case, a better reproducibility of the strength must be expected according to the views of Prof. Joffé.

In a footnote at the end of his paper*, Prof. Smekal asserts that the temperature-dependence of plasticity, as derived by myself from the Becker formula, differs "only in externals" from a form given previously by him. Contrary to this, my conception of plasticity is radically different from that represented by Prof. Smekal; moreover, in my paper (*Z. f. Phys.* **89** (1934), footnote on p. 657) I showed that his fundamental assumptions are inadmissible.

Prof. A. SMEKAL. Contrary to Dr Orowan, I must insist on my statement, that his interpretation of the temperature-dependence of plasticity differs only in externals from mine. The fundamental fact, that plasticity processes start or proceed always on crystal flaws with local stress maxima of the order of magnitude of ideal lattice cohesion—which we proved by rock-salt experiments—is adopted by Orowan without alteration. Again, Orowan uses the assumption that the thermal energy demanded for this process is greatly reduced by the local supply of elastic energy of the stress concentrations on the flaws. Indeed, only these two facts are required for a qualitative understanding of the temperature-dependence of plasticity. In my papers it is stated that the effective elastic energy concentration belongs primarily to single particles of crystal flaws. On the contrary Orowan desires to use the Becker formula, which concerns only homogeneous strain within finite volumes of flawless, ideal lattices; Orowan assumes that homogeneous strain within finite volumes of lattice may be realized also at the actual crystal flaws, so that the elastic energy supply belongs according to him to a multitude of particles. Obviously this assumption is in contradiction to stress concentration on the flaws, necessarily connected with inhomogeneous stress distributions around the flaws, giving the maximum stresses on single particles. The claim of Orowan, that he has shown the inadmissibility of my fundamental assumptions on a diffusion mechanism of plasticity, seems to be just as erroneous, as his criticism disregards all decisive arguments.

Sir ROBERT ROBERTSON. I might amplify the remarks made by Sir William Bragg and by Prof. Andrade on the subject of the two types of diamond that have been discovered by my colleagues and myself.

The failure to give an absorption band at 8μ in the infra-red in the case of one particular diamond, and its much greater transparency in the ultra-violet when compared with a large number of diamonds all of which gave a large absorption band at 8μ , led to an investigation of the physical properties of the two types, an account of which will be found in *Phil. Trans. Roy. Soc. A*, **232**, pp. 463 to 535. (See also *Nature*, **134**, 485 (1934).)

Besides being more absorptive, the ordinary type is more anisotropic and has very much less photoelectric conductivity than the less usual type. Both types have in common the same Raman difference, dielectric constant and refractive index.

* P. 108.

A large electric current is produced with the less usual type, by the imposition of short length ultra-violet light (max. λ 2300). A diamond thus activated responded to green or red light (max. λ 5850), even after it had been kept for a considerable time in the dark; but if in the meantime light of wave-length of λ 2400 to λ 5000 had been imposed on the diamond previously activated by light of λ 2300, no response was obtained by the red light.

It was observed that this photo-electric effect occurred in diamonds which appeared to be laminated. Indeed, the search for others, five now having been obtained, was conducted by looking for such diamonds as were obviously finely stepped. A coarse stepping is common among natural diamonds, but this was of no importance.

As has been shown on the screen by Prof. Andrade, the photo-conductive diamonds are those which he has shown by his technique to be more striated than the ordinary sort.

In the paper referred to, the comparatively easy production of photo-electric currents is considered to be connected with the mosaic structure of these stepped or laminated crystals, the atoms at the boundaries of the irregularities being thought to lose electrons more readily than those in the uninterrupted lattices. It was therefore of great interest to see the model produced by Sir William Bragg to account for these irregularities in the major structure of diamond.

Prof. A. SMEKAL. I should like to give some additions and corrections to the papers of Joffé. There are or were many differences of interpretation and also differences concerning experimental facts. We have repeated a number of the experiments of the Joffé school and have found somewhat different results. For simplification, it will be sufficient to deal on this point only with the strength of rock-salt crystals. Contrary to Joffé, rock-salt has no standard strength, neither in air⁽¹⁾ nor in water⁽²⁾, nor in vacuum⁽³⁾. The strength is not independent of temperature⁽⁴⁾ nor of velocity of deformation⁽⁵⁾. Lastly, rock-salt is not brittle at ordinary temperature, but possesses a characteristic plasticity⁽⁶⁾. On other points we are in agreement with Joffé, namely on facts which were found and published in my laboratory before the Russian school, for instance on the increase of faults by plastic deformation⁽⁷⁾, on the photoelectric determination of limit of elasticity⁽⁸⁾ and on the existence of a kind of dissociation along the gliding planes.

Concerning his experiments for the realization of the theoretical lattice strength, Joffé now agrees that his results are plasticity-effects. His original aim of realising the lattice strength on a brittle state of a crystal therefore could not be established. I hope it is now generally accepted from these experiments that the rise of the strength to the order of magnitude of the lattice strength results from the destruction of the monocrystalline state by plasticity.

Special reference is necessary to the statements of Joffé on rock-salt crystals where the surface was dissolved by water. In his paper Joffé speaks only of solution during loading experiments and claims that he has disproved my water-penetration explanation of the watering plasticity, by experiments on partially protected crystals

given by Classen-Nekludowa. But the lack of penetrated water on the protected side must prevent the rise of complete gliding planes, necessary for the ordinary watering-plasticity of crystals; the observed fact, that the strength remains unchanged in this case, is then by no means inconsistent with the water penetration theory. Moreover, the presence of water in the interior of dissolved crystals was demonstrated spectroscopically by Barnes. A saturated solution of salt gives neither solution- nor strength-effects in solution. On the penetration theory, contrary to the opinion of Joffé, only very slow penetration, or no penetration at all, of water molecules into the rock-salt is expected in this case.

The statement of Joffé that our own experiments had changed my opinion on my theory is incorrect. We have recently made dissolving experiments without mechanical deformation of crystals and have measured the effect of watering on the strength, after drying the surface with concentrated alcohol⁽⁹⁾. Wendenburg, in my Institute, used different solvents and found different after-effects, clearly connected with the different dipole-moments of the solvent molecules⁽¹⁰⁾. Roeber, also working in my Institute, has found that the after-effect increases systematically with the time of solution, and exhibits very interesting changes with the time which elapses between drying and carrying out the mechanical experiment. The strength of crystals decreases first to a minimum situated above the strength of undissolved crystals, then it rises to values much higher than the initial⁽¹¹⁾. All these observed facts are consistent only with a penetration theory, which seems in this way directly established.

Another point of difference is the statement of Joffé that the practical weakness of crystals cannot be influenced by internal faults. This statement can only be accepted in a very restricted form, as we have proved by experiments on rock-salt crystals with various foreign atoms. If we suppress the plasticity of rock-salt by means of very low temperature, the strength is generally diminished by increase of internal flaws⁽¹²⁾.

Crystals with as many faults as rock-salt exhibit fine-stepped cleavage planes by interferometric observation, and so make it directly visible that the strength is influenced by a great number of internal flaws⁽³⁾. Only in the limiting case of crystals with few faults is the influence of flaws situated on the surface naturally predominant, as Joffé has indicated. Experiments of the late Lord Rayleigh and more recently by Bond and by Siegbahn on cleavage strips of mica have given only a few steps and prove then the presence of only a few internal flaws for these crystals. In accordance with this fact, the strength of mica found by Orowan is only ten times less than the expected value of the theoretical lattice strength⁽¹³⁾.

There is no doubt that the splendid experiments of Griffith on the strength of glass and his theory of the breaking stress have been the most striking suggestions for all later experiments on the strength of glass and crystals. I would like to express my agreement with Griffith that his treatment of a single flaw of elliptic cross-section was and is only the first step to a general theory of stress-concentration in bodies with any flaws and its relation to breaking stress problems. This generalization seems to be necessary because all quantitative applications of the Griffith

theory, excepting only his original experiments, are not in full accordance with experimental facts. I should like to indicate here only the breaking of glass rods. Our experiments gave, contrary to Joffé, breaking surfaces, which often started from internal flaws⁽¹⁴⁾, and breaking stresses, depending for certain glasses on temperature⁽¹⁵⁾. The most striking point is this. The breaking surface of glasses consists of a smooth mirror-like part and another uneven part. For rods of the same cross-section, and under the same conditions of experiment, the mirror-like part is found of very different magnitude⁽¹⁶⁾. On the Griffith theory the breaking surface should always be mirror-like over the full cross-section. We see, also, that the breaking process in glass never depends on a solitary surface flaw.

What I said on these facts refers also to various statements in Orowan's paper. In connexion with my name, this paper deals with matters which were not given by me and for which I am not responsible. In particular, I have never proposed a block theory of strength, of the type indicated by Orowan⁽¹⁷⁾, which is completely contradictory to our own experiments. To establish this it should be sufficient to compare Orowan's paper with mine.

REFERENCES

- (1) F. BLANK. *Z. f. Phys.* **61**, 727 (1930); H. SCHÖNFELD, *ibid.* **75**, 442 (1932).
- (2) U. HEINE. *Z. f. Phys.* **68**, 591 (1931); G. F. SPERLING, *ibid.* **74**, 476 (1932).
- (3) W. BURGSMÜLLER. Thesis, Halle, 1935.
- (4) W. BURGSMÜLLER. *Z. f. Phys.* **80**, 199 (1933); **83**, 317 (1933).
- (5) G. F. SPERLING. *loc. cit.*; D. MAHNKE, *Z. f. Phys.* **90**, 177 (1934).
- (6) F. BLANK. *loc. cit.*; W. THEILE, *Z. f. Phys.* **75**, 763 (1932).
- (7) A. SMEKAL. *Wien. Akad. Anz.* **22**, 46 (1927).
- (8) H. J. SCHRÖDER. *Z. f. Phys.* **76**, 608 (1932); A. SMEKAL, *Phys. Z.* **34**, 633 (1933).
- (9) A. SMEKAL. *Wien. Akad. Anz.* (1928), p. 62; *Naturwiss.* **16**, 262 (1928); *Phys. Z.* **32**, 581 (1931).
- (10) K. WENDENBURG. *Z. f. Phys.* **88**, 727 (1934).
- (11) J. ROEBER. *Z. f. Phys.* 1935 (in course of publication).
- (12) W. BURGSMÜLLER. *Z. f. Phys.* **83**, 317 (1933).
- (13) A. SMEKAL. *Handbuch der Physik*, 2nd ed. **24**, 2, pp. 919-20 (1933).
- (14) K. H. H. MÜLLER. *Z. f. Phys.* **69**, 431, § 4 (1931).
- (15) K. H. H. MÜLLER. *loc. cit.* § 7.
- (16) K. H. H. MÜLLER. *loc. cit.*; G. APELT, *Z. f. Phys.* **91**, 336 (1934); G. THIERBACH, *ibid.* **91**, 344 (1934).
- (17) Orowan also fails to indicate the *ideal* connexion between lattice blocks, mentioned in one of my oldest papers, and making this conception equivalent to the gap crystal model.

Dr A. JOFFÉ. I should like to avoid a discussion of Prof. Smekal's declarations of priority and of the historical development of the investigations on rock-salt. I do not deny that some of my ideas suggested by our investigations of rock-salt in the years 1919 to 1923 were changed by new experimental facts found both in my laboratory and by the school of Prof. Smekal.

As far as I can see, the objections of Prof. Smekal can be summarized in the following four statements:

1. The strength of rock-salt depends on temperature.
2. Rock-salt is already plastic at room temperature.
3. The high strength of wet rock-salt is only due to plastic deformation.

4. Wet rock-salt becomes plastic by penetration of water and not by a change of the surface.

1. It may be that the approximate constancy of the brittle strength of rock-salt (within ± 10 per cent) is not present in samples of different origin. The strength curve may be somewhat concave in those cases. All that is essential for my presentation of a brittle and plastic state is a crossing of this curve with the steep curve representing the dependence of the yield limit on temperature. In no case is it permissible to combine in one curve the brittle rupture at low temperatures with the plastic rupture at high temperatures. Similarly, Smekal's curve representing the strength at a given velocity of deformation between liquid air and $+500^{\circ}\text{C.}$, or a curve of "Dauerfestigkeit," is meaningless from a physical point of view. These are different systems of representing measurements, which may become useful when some new physical idea has appeared. If Prof. Smekal could realize at higher temperatures the value for brittle rupture as the lower limit of the strength at increasing velocity of deformation he would find my results with more or less accuracy.

2. It is true that the elastic limit of annealed rock-salt is as low as 10 gr./mm^2 , while rupture occurs at $300\text{--}400\text{ gr./mm}^2$. It is also true that by exceedingly slow deformation during 100 hours I was able to bend a rock-salt crystal under room temperature. Nevertheless the rupture of rock-salt at room temperature at ordinary conditions can be regarded as a brittle one, as it appears before the yield point shown for instance by X-ray asterism and by the flow of material is reached. Both pure brittle rupture and plastic distortion are limiting cases (important, as I tried to show, for the understanding of the physical phenomena leading to a breakdown). Though there is a continuous change from one to another, at a definite stage of this change we meet a new situation, where the essential features become different. Changes produced by gliding below the yield point do not alter the obviously brittle character of the rupture of dry and cold rock-salt.

3. The high strength of rock-salt measured in water is observed in an already plastically deformed crystal. The essential point is however the high magnitude of the cohesion forces, leading to a high strength when secondary phenomena are avoided. This is shown to be true whether we deal with single crystals like quartz and mica, with multicrystalline bodies like rock-salt and steel, or with an amorphous material like glass or amorphous silica. In all cases we do actually increase the strength by suitable treatment of the surface and the theoretical strength is the more nearly reached the more completely all secondary influences are removed.

4. I am sorry if I have misunderstood one of the various statements made by Prof. Smekal*: "Whether the high plasticity of wet rock-salt can find sufficient explanation by these results (penetration of water), I regard as uncertain." Prof. Smekal then suggests two other explanations which agree with my statements in the only essential point, namely, that water eliminating surface disturbances leads to a markedly higher tensile strength. As the yield points of dry and wet rock-salt are equal, it seems that some increase of strength by removal of surface imperfections

* *Phy. Rev.* **43**, 306 (1933).

must be assumed in order to understand how the plastic flow of wet rock-salt starts. Both the absence of any influence of saturated salt solution and the experiments of Classen-Nekludova and Davidenkov show that surface conditions are important for this first step in the plasticity of rock-salt crystals in water. From hundreds of samples taken from a water bath, some lost their plasticity after a few seconds and some after many days. How could water disappear from all the imperfections inside the crystal during a second?

I did not understand the explanation of the experiments of Classen-Nekludova given by Prof. Smekal. Why did not water penetrate from inside to the protected strip after solution of the greater part of the crystal? The experiment shows that a small dry spot on the surface is more important than the penetration of water into the crystal.

New experiments on this subject mentioned by Prof. Smekal should be very interesting and should help us to understand the influence of water on rock-salt, but I do not think they will alter the fact that a change of the surface conditions is essential for the rupture, just as it is in the case of glass, steel and quartz.

Dr E. OROWAN. 1. Prof. Smekal asserts that, in connexion with his name, my paper deals with matters which were not given by him; he writes: "In particular, I have never proposed a block theory on the strength of crystals, which is completely contradictory to our own experiments."

I must, however, maintain the statement that Prof. Smekal suggested the block-structure hypothesis, referring expressly to the problems of mechanical strength, especially to the discrepancy between theoretical and technical strength. In his paper referred to in my contribution, he wrote*: "Bestehen die Gitter der wirklichen Krystalle hingegen aus sehr zahlreichen submikroskopischen, im Sinne der Bornschen Theorie ideal-regelmässigen, nahezu gleich orientierten 'Gitterblöcken,' welche das Zustandekommen von Störungszonen und Porenwegen ermöglichen, so gelingt es, die aufgezählten Schwierigkeiten [amongst other things, the discrepancy between theoretical and technical strength—Orowan] zu überwinden, ohne damit auf die bisherigen Erfolge der Bornschen Gittertheorie verzichten zu müssen.—Bezüglich der Festigkeitseigenschaften der Krystalle ergibt sich vor allem die bereits früher angegebene Aufklärung der niedrigen 'technischen Festigkeiten'...."

This paper of Prof. Smekal was, as a matter of fact, the starting-point of a block structure explanation of mechanical strength as described in my paper, which became very widely spread in the subsequent years, especially amongst mineralogists and metallurgists, without being disavowed by Prof. Smekal himself until now. The experiments he refers to were performed later and published without pointing out that they are in contrast with the common views on block structure hypothesis.

2. Recently I showed† that the penetration hypothesis of the Joffé effect, as advocated by Prof. Smekal in his contribution to this discussion, cannot be main-

* *Wien. Anz.* p. 192 (1925).

† *Z. f. Phys.* 86, 210 (1933).

tained. A simple calculation, using an experimentally determined lower limit for the speed of solution of rock-salt in water, gives an upper limit for the depth at which water becomes practically saturated when penetrating into invisible crevices of such a crystal. This upper limit is $1/10$ mm. if a saturation amounting to $999/1000$ is required. Since a surface layer of 0.4 to 0.5 mm. at least has to be dissolved before an appreciable increase of strength appears, the interior of a crystal showing the increased strength has never been in contact with solution other than saturated. Now it is well known that immersion in a saturated solution does not produce any trace of a Joffé effect; thus this effect cannot be caused by a penetration of the solvent into the interior of the crystal but by a surface action only*.

This inference is supported by the following observation of Wendenburg (*loc. cit.*): If a sufficiently thick surface layer of an unloaded rock-salt crystal is dissolved, then after drying the crystal shows a Joffé effect of the usual order of magnitude. Its strength diminishes somewhat in course of time; yet it reaches asymptotically a final value which is still of the same order of magnitude. Obviously the only explanation of the Joffé effect which is in accord with this behaviour is that given by Joffé himself (removal of surface cracks by solution as the cause of the effect). That the strength obtained and the final strength vary slightly with the nature of the solvent is considered by Wendenburg and by Prof. Smekal as a support to the penetration hypothesis. This standpoint, however, seems to be forced; it is, indeed, a very general feature of etching, which plays a fundamental rôle in metallography, that the coarseness of an etched surface depends upon the nature of the solvent.

The fact that there is, besides, a connexion between the increase of the strength and the dielectric constant of the solvent, is also considered by Prof. Smekal as a support to his hypothesis. This influence is, however, most probably due to the fact that the strength of a body is *lowered* if a fluid penetrates into its cracks, in consequence of the decrease of its surface energy by adsorption†. This means that the action of the penetrating fluid is inverse to what is supposed by the penetration hypothesis.

Mrs C. F. TIPPER (Miss ELAM). I should like to give two examples of structures in crystals which seem to support Goetz's experimental results and are related to yesterday's discussions.

1. The first illustrates the laminated structure produced on a polished surface of copper when a fully annealed specimen is heated *in vacuo* at 950° C. A similar structure was described by Rosenhain in silver some years ago. The laminations are definitely related to the crystal structure and very much resemble slip-bands. On the other hand they are frequently curved, even in fully annealed material.

2. The second refers to the etch figures on calcite. The size of the etch figures

* The objection made by Wendenburg (*Z. f. Phys.* **88**, 727 (1934)) emphasizing that a saturated solution may not penetrate at all into the crystal is obviously unsafe; with his assumption, the penetration hypothesis would *a fortiori* be illusory.

† Cf. E. Orowan, *Z. f. Phys.* **86**, 206 (1933).

produced by dilute hydrochloric acid on the surface of a cleavage rhomb differs from crystal to crystal. When such a rhomb is twinned mechanically in the manner described by Baumhauer, the size of the etch figures is much smaller on the surface of the twinned portion than it is on the original surface. This indicates a breaking-up of the crystal structure, although crystallographers state that the twinning is perfect.

Dr A. E. H. TUTTON. As one of the "old gang," to which Lord Rutherford referred at the morning session, I am very glad to learn that Prof. Ewald has succeeded in obtaining the perfect crystal of sodium chloride, and that he has found it to afford the data which he has expected, and which fulfilled the predictions of Prof. Darwin for the perfect crystal.

We have heard much to-day concerning "Krystallbaufehler," and also much of late concerning the "ideally imperfect" crystal, the "mosaic crystal," which has answered so admirably the purposes of the X-ray rotation method of crystal analysis. I myself have been combating for many years the "mosaic crystal," so unsuitable for crystal measurement and crystal optics. For of the 36 years which occupied me in the work on the rhombic sulphates and selenates of the alkalies, and on the monoclinic double sulphates and selenates containing $6\text{H}_2\text{O}$, quite half the time was taken up in preparing perfect crystals, affording crystal angles true to within one minute of arc, free from mosaic or any other imperfections, by using only material of perfect chemical purity, and eliminating all sources of disturbance, thermal or otherwise. Often as many as a hundred crops of any one of the 91 salts were prepared, and only one or two found adequately perfect for my purpose and used in the investigation. Hence, it is possible for me to have a very special appreciation of Prof. Ewald's success, and a great satisfaction that it has afforded such excellent results in confirmation of theory.

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PLASTICITY AND STRAIN HARDENING
IN CRYSTALS

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SHEAR HARDENING AND RECRYSTALLIZATION OF ALUMINIUM SINGLE CRYSTALS

WITH AN APPENDIX ON "TRANSFORMATION HARDENING"

By W. G. BURGERS

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Eindhoven, Holland

ABSTRACT. The paper is a review of an extensive series of investigations on the deformation and recrystallization of aluminium crystals.

It is pointed out that when a crystal undergoes plastic deformation it is hardened, the shear resistance increasing considerably. All recent theories on the origin of this effect agree that the macroscopic glide process consists essentially of the combined effect of a large number of "local glide steps," which are related to the deviations from the ideal lattice structure.

A homogeneous shear distortion can be produced in a circular disc cut out of an aluminium single crystal plate if it is compressed with certain precautions. Nevertheless, Laue photographs show the presence of "curved" lattice regions, the curvature having a definite crystallographic direction. This implies that slip has occurred over *limited* regions of the slip planes.

Again, if gliding occurs along more than one set of planes, then local curvatures occur along each operative system.

The picture thus formed of the inner structure of a "homogeneously" deformed single crystal can be, at least partially, confirmed by studying the recrystallization process. In fact, the nuclei for the small crystallites formed by recrystallization occur at the local curvatures of the glide planes, so that the crystallites occupy a definite preferred orientation determined by the glide processes which occurred during the deformation. Moreover, if two crystals have undergone the same shear hardening, one by shear along a single glide plane, and the other by shear along more than one, then there is a difference in recrystallizing power; there are less nuclei in the case where more glide planes have been in operation.

In an experiment which illustrates this, aluminium single crystals were stretched 10 per cent parallel to the $[100]$ and others parallel to $[110]$ direction. Measurement showed that their hardening was practically the same, but on recrystallization, there were practically no crystals formed in the first case, whereas, in the other case, the crystals became fine-grained. This agrees with the fact that in the first case the local curvatures are smaller than in the other, implying that the total shear has then been divided over more glide planes.

The appendix deals with transformation hardening, which occurs on transition of one phase of a solid metal into another. Here the new lattice is formed from the old by a homogeneous deformation consisting of one or more simple shears combined with small dilatations or contractions. It differs markedly from the processes previously considered, in that, in this case, the transformation process may cause the specimen to become harder, unlike a strained test-piece, which becomes annealed on recrystallization.

IN the present paper a review is given of the results obtained during the years 1928–1933 in a series of investigations on the deformation and recrystallization of aluminium crystals, the details of which have been published elsewhere.

(1) It is a well-known fact that the “strength” of an undeformed crystal is of a lower order of magnitude than would be anticipated from theoretical considerations regarding the forces which hold the atoms or ions in crystalline lattices together. Such considerations have been put forward especially by Joffé, Smekal and Zwicky* for ionic crystals like rock-salt, and by Polanyi and Schmid† for metal crystals.

If, however, a crystal undergoes plastic deformation, it hardens, the hardening process effecting an increase of the shear resistance of the not-hardened crystal from its extremely low value to a value, which, at its highest, is of the order of magnitude anticipated from the above-mentioned theoretical considerations regarding the atomic forces.

Several theories‡ have recently been put forward to account for the above-mentioned characteristic features of crystalline plasticity. They may be said to have in common the fundamental conception that the macroscopic “glide process” consists essentially of the combined effect of a large number of “local glide steps,” the occurrence of which is closely related to the presence, even in the undeformed crystal, of some kind of deviations from the “ideal” lattice structure. Although the various theories differ apparently regarding the exact nature of these deviations (“Lockerstellen” (Smekal), “dislocations” (Taylor), “Versetzungen” or “Verhakungen” (Polanyi; Orowan, Dehlinger)) and as to the way in which they initiate slip (as a consequence of local stress concentration or of special conditions of potential energy), their conceptions agree in so far that local glide steps occur under the influence of shear forces, which, while being originally small compared to that expected for an “ideal” lattice, increase with the number of deviations§.

The hardening process is, therefore, essentially connected with the increasing distortion of the deformed crystal. In case a crystal is subjected to a shear deformation, which, as to its *outer* form, is homogeneous over its full extent, this distortion must be related in some way to the “limited” character of the individual glide steps. The knowledge of the “internal distortion” of a “homogeneously” deformed crystal is thus important for the understanding of the glide phenomenon as a whole. It is the object of the present paper to show that some insight into this state may be obtained from a study of the recrystallization of single crystals which have been deformed in this way.

(2) If we cut a circular disc out of an aluminium single crystal plate (see Laue photograph, figure 3 *a*), and compress it between flat steel blocks with all necessary

* A. Joffé, *The Physics of Crystals* (1928); A. Smekal, *Phys. Z.* **34**, 633 (1933); F. Zwicky, *ibid.* **24**, 131 (1923); *Helv. Phys. Acta*, **3**, 269 (1930).

† M. Polanyi, *Naturwiss.* **16**, 1043 (1928); M. Polanyi and E. Schmid, *ibid.* **17**, 301 (1929).

‡ A. Smekal, *loc. cit.*; G. I. Taylor, *Proc. Roy. Soc. A*, **145**, 362 (1934); E. Orowan, *Z. f. Phys.* **89**, 605 (1934); M. Polanyi, *ibid.* p. 660; K. Yamaguchi, *Sci. Pap. Inst. phys. chem. Res. Tokyo*, **11**, 151, 223 (1929); see also U. Dehlinger, *Ann. d. Phys.* **2**, 749 (1929).

§ In *Proc. Acad. Amst.* (“Report on Viscosity”, Chapter v) is a suggestion how to combine the theories of Taylor and Orowan.

precautions for minimizing the resistance between blocks and disc, in the manner described by Taylor and Farren* (polishing and greasing of the disc, etc.), this disc takes an elliptical shape, indicating that, from a macroscopic point of view, a *homogeneous* shear deformation has taken place, in the way illustrated by figure 1 for a single glide plane.

This is confirmed by taking *rotation* photographs† of such a disc before and after compression. Two such photographs are reproduced in figure 2, *a* repre-

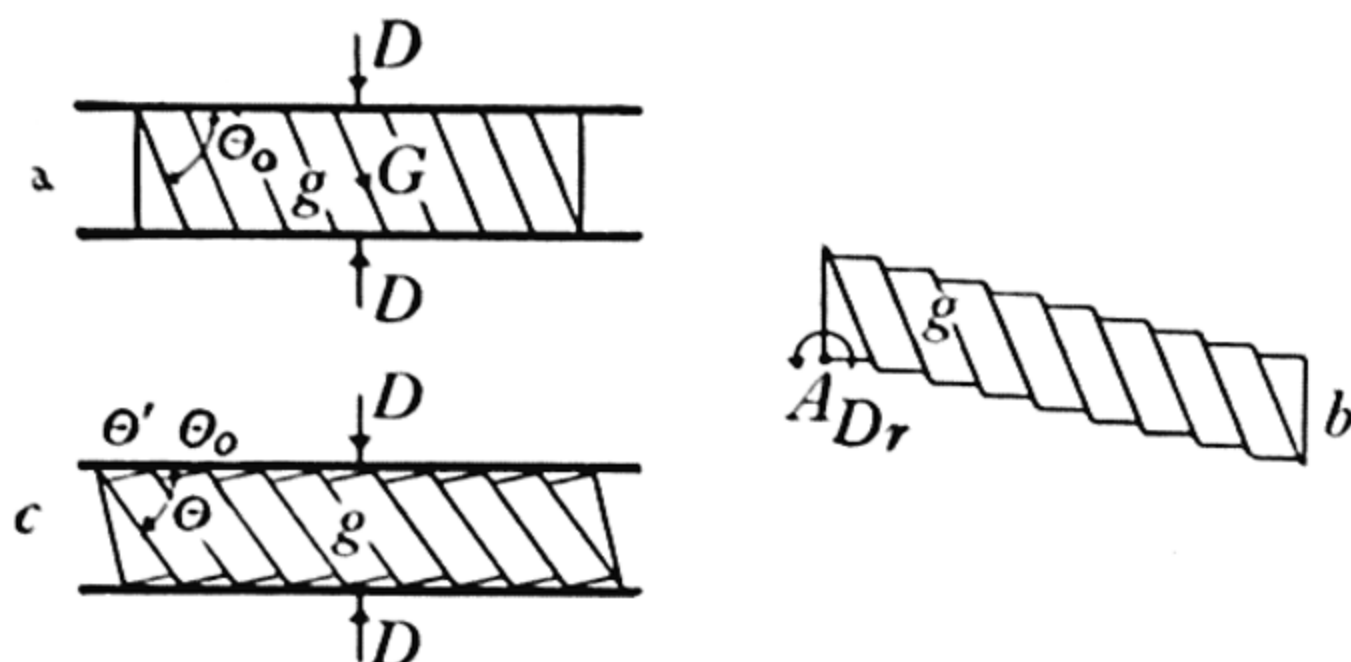


Figure 1. Change in orientation of glide lamellae during compression of a disc, cut from a single crystal.

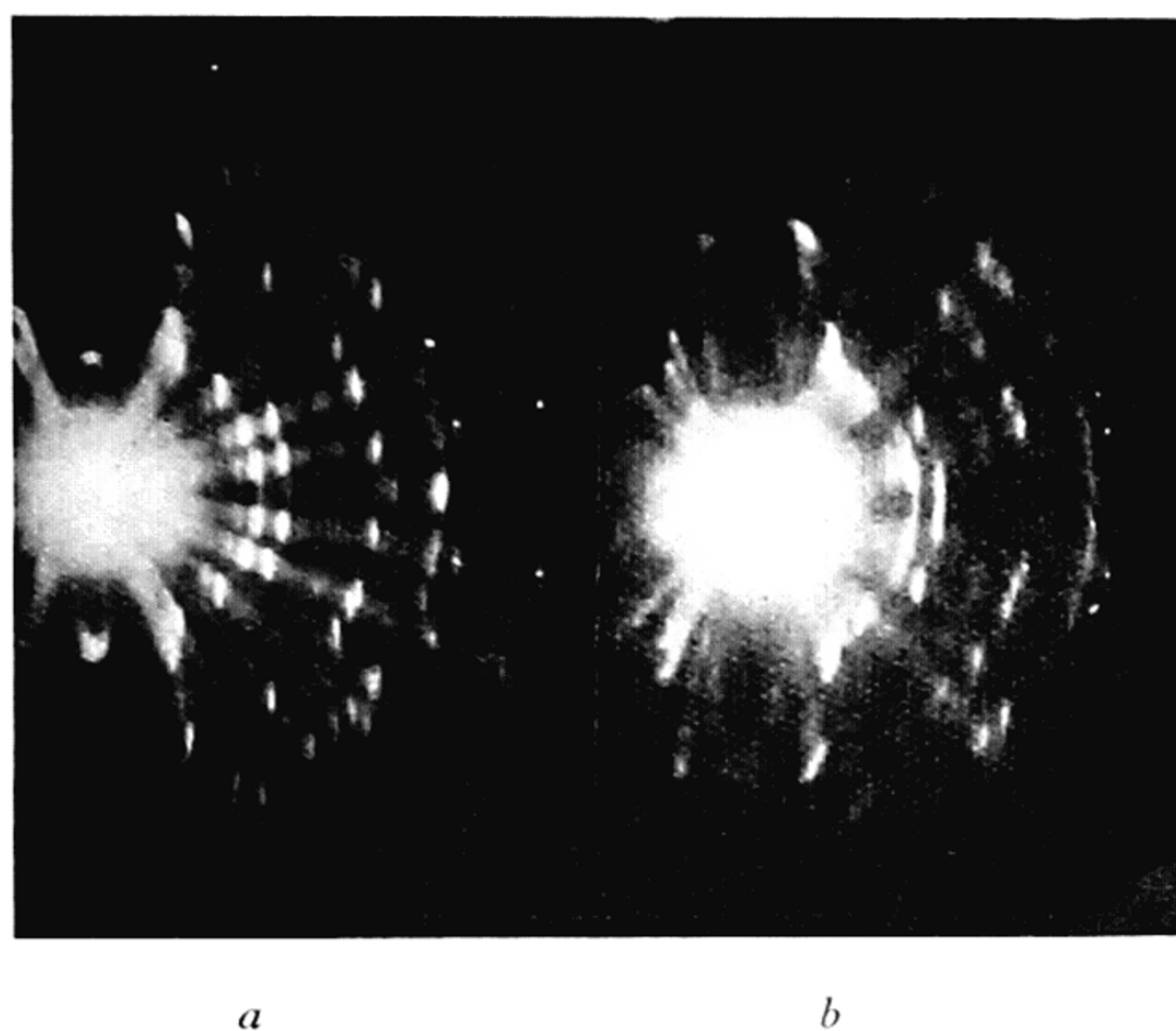


Figure 2. X-ray rotation-photographs of an aluminium single-crystal disc: *a* before compression; *b* after compression to about 0.8 of its original thickness.

sents the undeformed crystal, *b* after compression up to $d/d_0 =$ about 0.8. The fact that the spots on this last photograph are but little less sharp than those on figure 2 *a* indicates that the compressed disc can still be considered as being practically a "single crystal." From the relative shift of corresponding spots on both photographs, it can further be concluded that the position of the crystal lattice with regard to the surface of the disc has changed exactly in the way required by

* G. I. Taylor and W. S. Farren, *Proc. Roy. Soc. A*, 111, 529 (1926); *A*, 116, 16 (1927).

† The discs were rotated about their normal as axis, the X-ray beam "skimming" the outermost zone.

the glide process illustrated in figure 1, namely by a *rotation* (not a curvature) of the whole glide lamellae about the axis A_{Dr} , the line of intersection of the glide plane g with the plane of the disc.

In this "ideal" shear deformation there is no reason for any distortion of the crystal lattice. A Laue photograph of the compressed disc (figure 3 *b*) shows, however, elongated spots, thus indicating the presence of "curved" lattice regions*. From a geometrical analysis of these Laue photographs† it can be deduced that the curvature has a definite sense, namely around an axis $[211]$, which lies in the glide plane (of general form (111)) perpendicular to the glide direction (of general form $[110]$); on the photograph this is shown by the fact that the spot (No. 11),

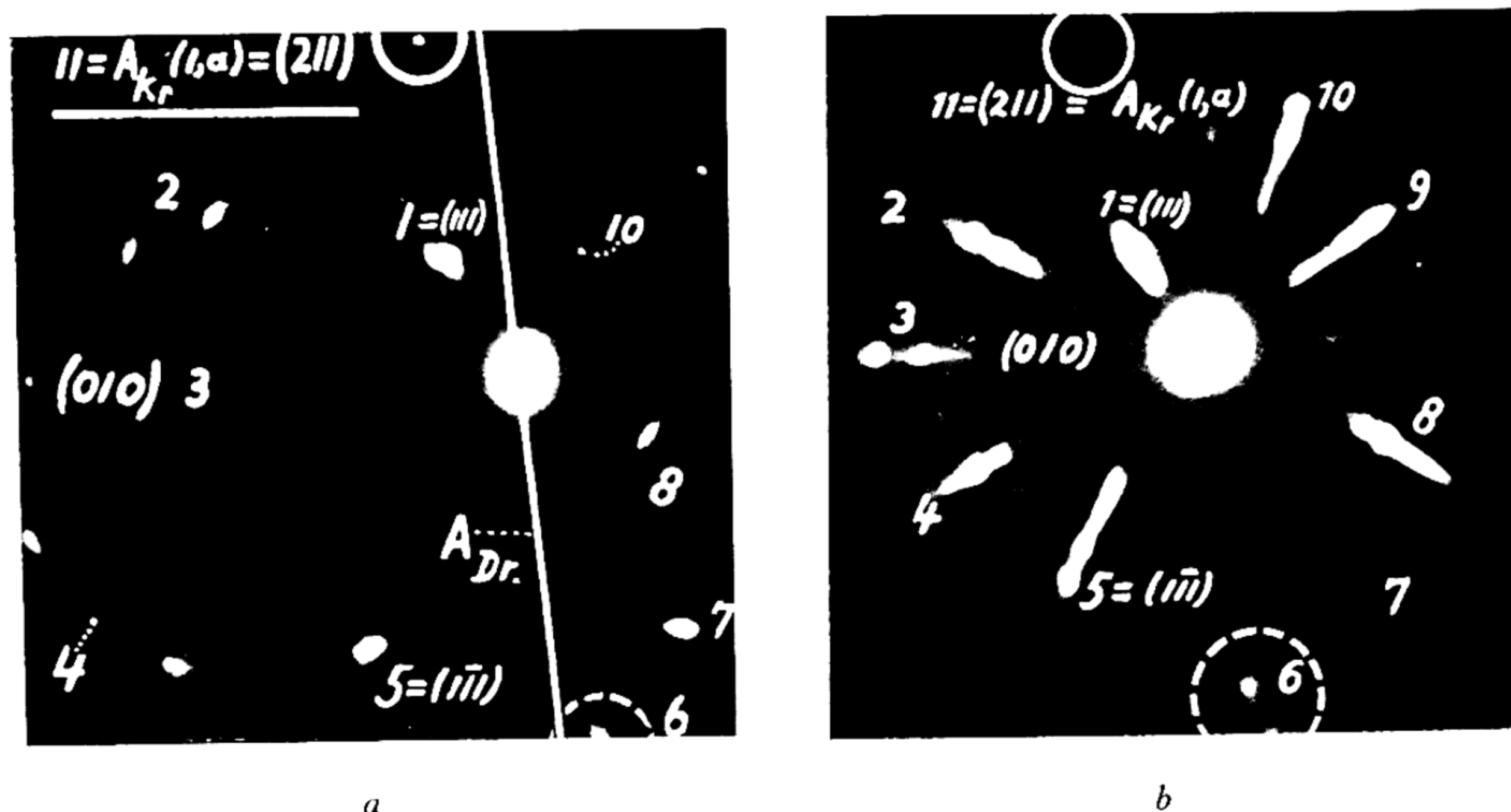


Figure 3. Laue photographs of an aluminium single-crystal disc. X-rays \perp disc-surface: *a* before compression (A_{Dr} = line of intersection of glide lamellae and disc-surface (compare figure 1)); *b* after compression to 0.86 of its original thickness.

due to reflection of the (211) -plane, which stands perpendicular to the first-mentioned axis, is practically not elongated on figure 3 *b*. It was found, further, that the degree of bending increases with the amount of shear along the glide plane.

In connexion with the homogeneous character of the deformation as a whole, the occurrence of lattice curvatures is only explicable if we assume, as has been done by Taylor and by Yamaguchi (*loc. cit.*), that they have a *local* character and are due to slip over limited regions of the slip planes. It seems probable that such "limited glide processes" are accompanied by local bendings of the glide lamellae around an axis which lies in the glide plane perpendicular to the glide direction (compare

* The occurrence of elongated spots on Laue photographs of deformed crystals and their connexion with the glide mechanism was first studied by J. Czocharlski (*Z. f. Metallk.* 15, 60 (1923)) and A. F. Joffé and collaborators (*Z. f. Phys.* 22, 286 (1924)).

† W. G. Burgers and P. C. Louwerse, *Z. f. Phys.* 67, 605 (1931); K. Yamaguchi, *Sci. Pap. Inst. phys. chem. Res. Tokyo*, 11, 151, 223 (1929); compare also G. I. Taylor, *Trans. Far. Soc.* 24, 121 (1928); H. J. Gough, Edgar Marburg Lecture, *Am. Soc. f. Test. Mat.* 33 (11), (1933).

figure 4, which is due to Yamaguchi, *loc. cit.*), that is exactly in the sense that can be deduced from the Laue photographs by purely geometrical analysis*.

We may perhaps get some insight into the "actual nature" of a local curvature by considering the fact that even a severely cold-worked aluminium test-piece, be it a single crystal or poly-crystalline, does not show an appreciable broadening of the Debye-Scherrer interference lines†, from which it can be concluded that the actual distortion has such a character that only a relatively small proportion of all the atoms has undergone irregular displacements from ideal lattice-positions. It

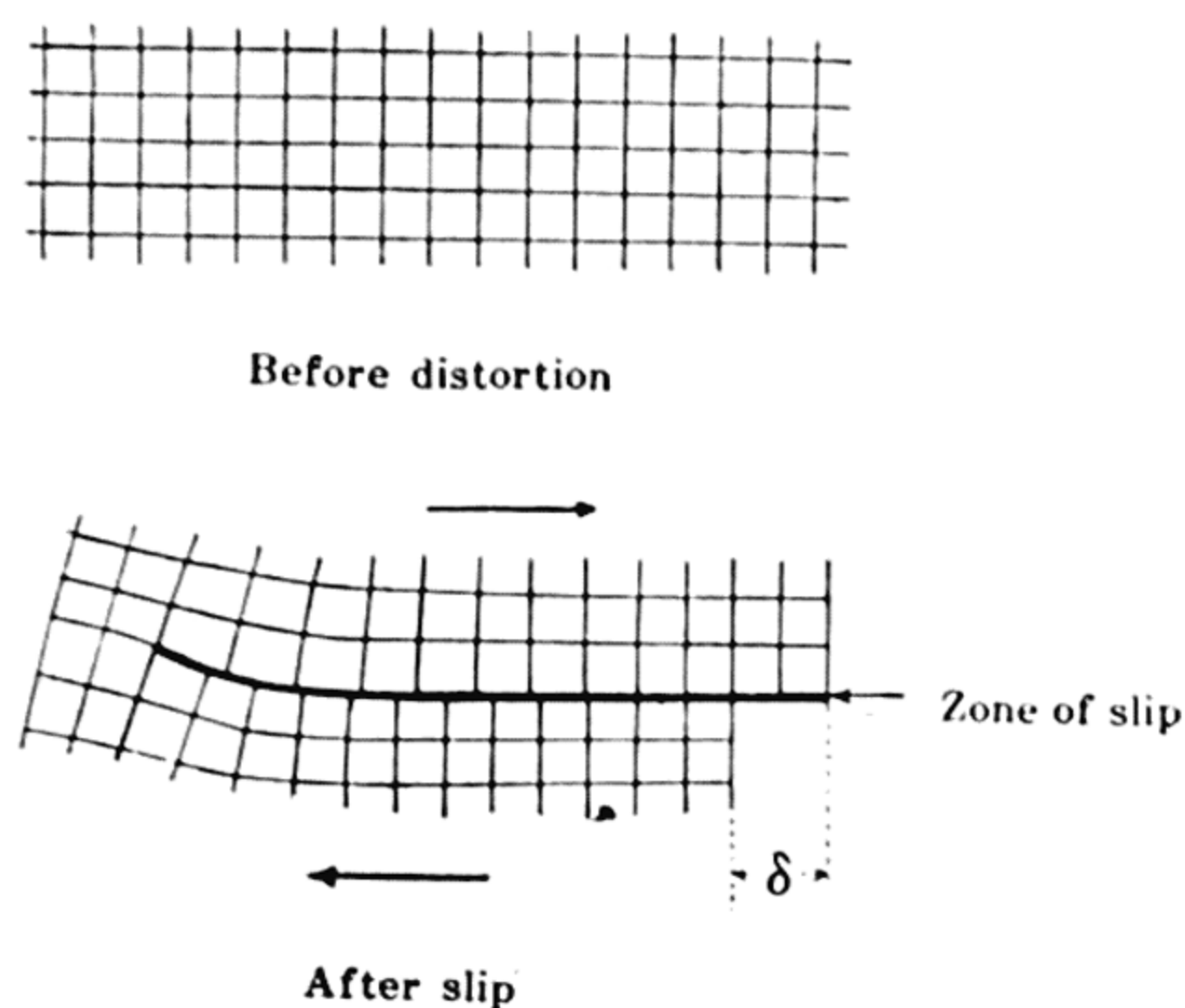


Figure 4. Schematic representation of a "local curvature" of the crystal lattice, due to slipping over a limited area. (After Yamaguchi.)

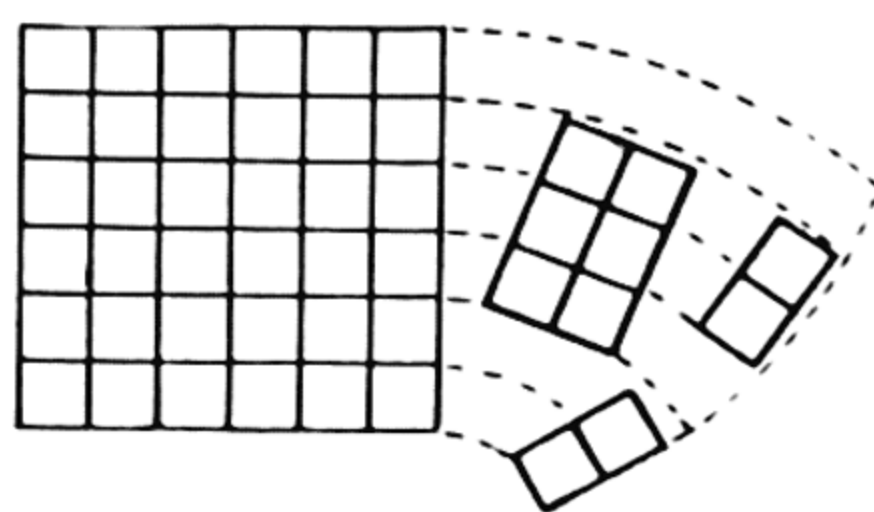


Figure 5. Schematic representation of "crystal break-up" in a "local curvature" along a glide-lamella of a deformed aluminium crystal.

seems probable, therefore, that a local curvature corresponds more or less to a "broken-up" crystal-region as shown schematically in figure 5, where the greater part of the atoms belong to undistorted or only slightly distorted lattice regions (thick lines), which are "glued together" by severely distorted regions (dashed lines)‡.

So we arrive at the conception of a uniformly distorted single crystal, in which gliding along one system of parallel glide planes has taken place, as shown schematically in figure 6 *b*, where the local curvatures are indicated by short thick

* See also the micro-photographs in Yamaguchi's paper: *Sc. Pap.*, etc. 8, 289 (1928).

† U. Dehlinger, *Z. f. Krist.* 65, 615 (1927).

‡ Compare H. J. Gough, *loc. cit.* figure 52; see also W. G. Burgers and P. C. Louwerse, *loc. cit.* p. 613.

lines*. Their "sense" corresponds to the rotations, which occur at the ends of a crack in an elastic material on applying shear parallel to the crack†. In case of gliding along more than one set of planes, it may be expected, and it is *confirmed by analysis of the corresponding Laue photographs* (for the details of which we must refer to our paper, quoted on p. 142, footnote), that "local curvatures" are formed along each of the systems of glide planes, which have taken part in the deformation process, in the way represented schematically in figure 6 *c* for two glide planes.

Now it is reasonable to assume that the "local curvatures" as a consequence of "overlapping" of atom-rows are closely related to the "dislocations" or "Versetzen" ("Verhakungen") considered by various authors in their theories of plastic deformation, and are thus essentially connected with the hardening of the

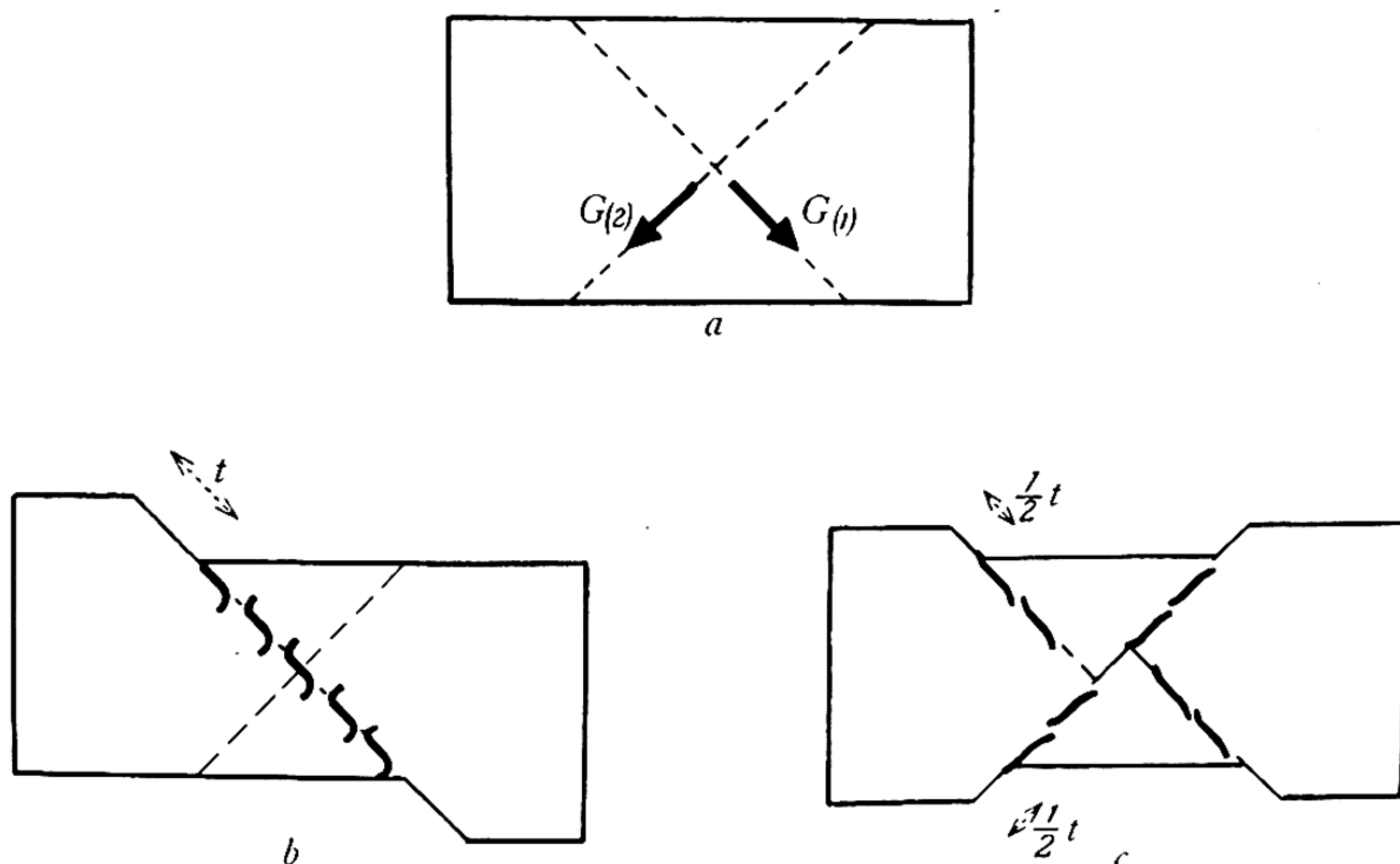


Figure 6. Schematic representation of "local curvatures" along glide planes: for a given *total* shear t the average degree of bending is greater in case of gliding along one (figure 6 *b*) than along two (figure 6 *c*) glide planes.

crystal against further shear. As it is known from the investigations of v. Göler, Karnop and Sachs‡ and from those of Taylor§ that the shear hardening of aluminium single crystals practically only depends on the *total amount* of shear, independent of whether this has taken place along one or along two sets of glide planes, this means that *the same shear hardening can be effected by different "systems of curvatures,"* viz. by the system of curvatures represented schematically in figure 6 *b* (one glide plane, with a "small" number of "strong" curvatures) as effectively as by that of figure 6 *c* (two glide planes, with a "large" number of "weaker" curvatures).

* A similar schematic representation is given by H. J. Gough in his Edgar Marburg Lecture (*loc. cit.* figure 21).

† A. T. Starr, *Proc. Camb. Phil. Soc.* 24, 289 (1928).

‡ Frhr. v. Göler, R. Karnop und G. Sachs, *Z. f. Phys.* 41, 103, 116 (1927).

§ G. I. Taylor, *Proc. Roy. Soc. A*, 116, 39 (1927).

If we assume that the energy surplus (stress content) in a “strong” curvature is greater than in a “weak” curvature, we may picture in an energy diagram the two states of the deformed crystal, which relate to the *same* shear hardening, as is done schematically in figures 7 *a* and 7 *b*: in these figures the shaded areas represent the energy surplus in a “curvature”; *a* relates to gliding along one plane, *b* to gliding along two (eventually more) glide planes.

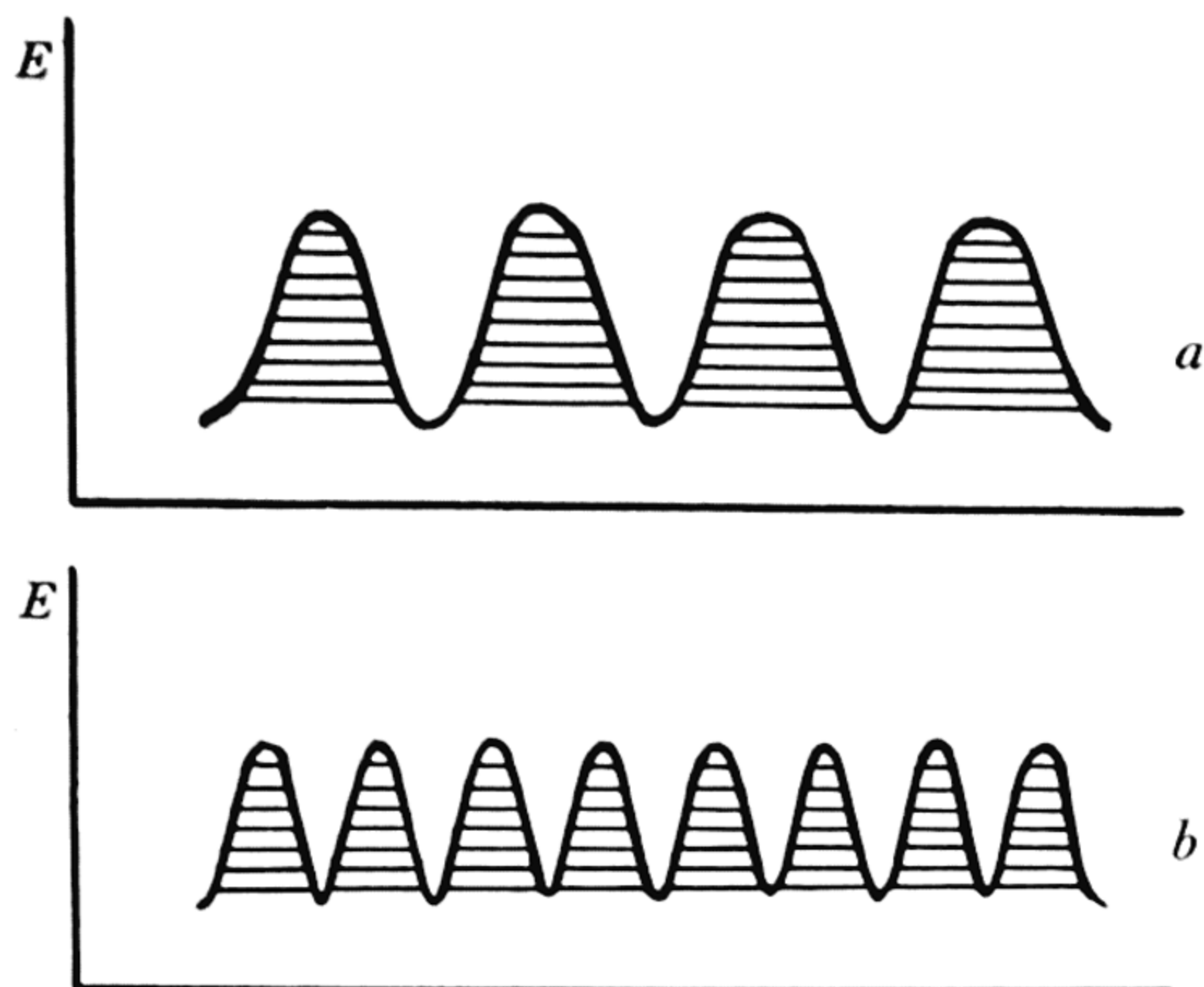


Figure 7. Schematic representations of the distribution of stress concentration in two states of a deformed crystal, relating to the same *total* shear (and thus practically the same shear hardening): *a* in case of gliding along one glide plane; *b* along two glide planes.

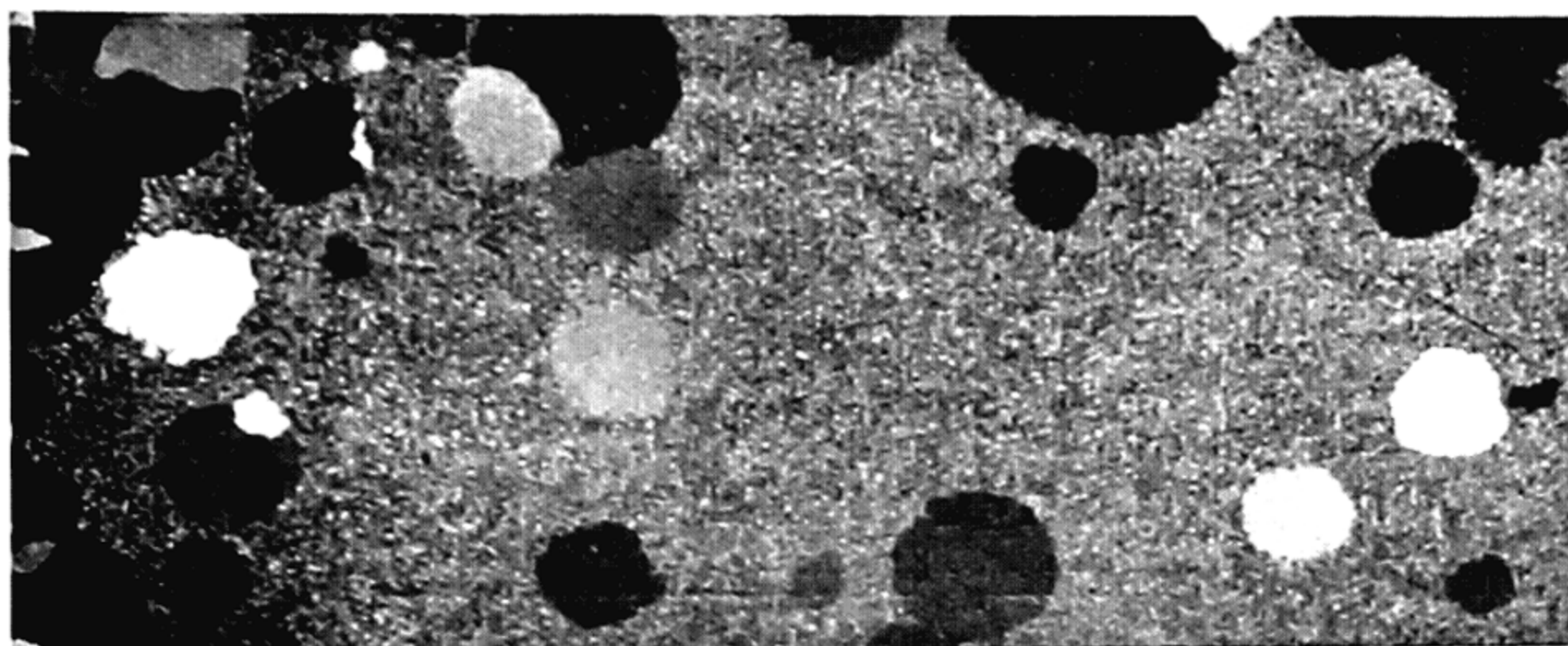


Figure 8. Recrystallization of a strained metal: the new undeformed crystals grow from nuclei.

(3) We shall now proceed to consider in what way the above picture of the “inner structure” of a “homogeneously” deformed single crystal can, at least to some extent, be confirmed by studying its recrystallization process.

Figures 8 and 9, which are due to van Arkel*, illustrate two characteristic features of the recrystallization process in general. They both relate to fine-grained aluminium test-pieces, which have been stretched a few per cent and then heated at 600° C. for a relatively short time. Figure 8 shows that the new undeformed†

* Compare A. E. van Arkel, *Polytechn. Weekblad*, 26, 397 (1932); *Z. f. Metallk.* 22, 217 (1930).

† Compare however p. 151.

crystals grow from definite nuclei, till they come into contact with each other. Figure 9 demonstrates how these nuclei are formed especially at those points of the deformed test-piece where the concentration of stress has been largest, as was the case in the neighbourhood of the incisions which were cut into the test-piece before stretching.

Applying these two well-known facts to the recrystallization of the homogeneously deformed aluminium single crystals, we may expect in the first place that the nuclei will be formed in the local curvatures of the glide planes. According to a point of view set forth by Dehlinger*, we may conceive this process as consisting of a "loosening" of the severely dislocated atoms (dashed lines in figure 5) between the more or less strain-free regions (thick-drawn lines in figure 5), followed by subsequent growth of these regions. If this is actually the case, then *it must be expected that there will be a definite relationship between the orientation of the mother crystal and that of the small crystallites formed by recrystallization of a homogeneously compressed aluminium single crystal*, in the sense that the new crystallites occupy

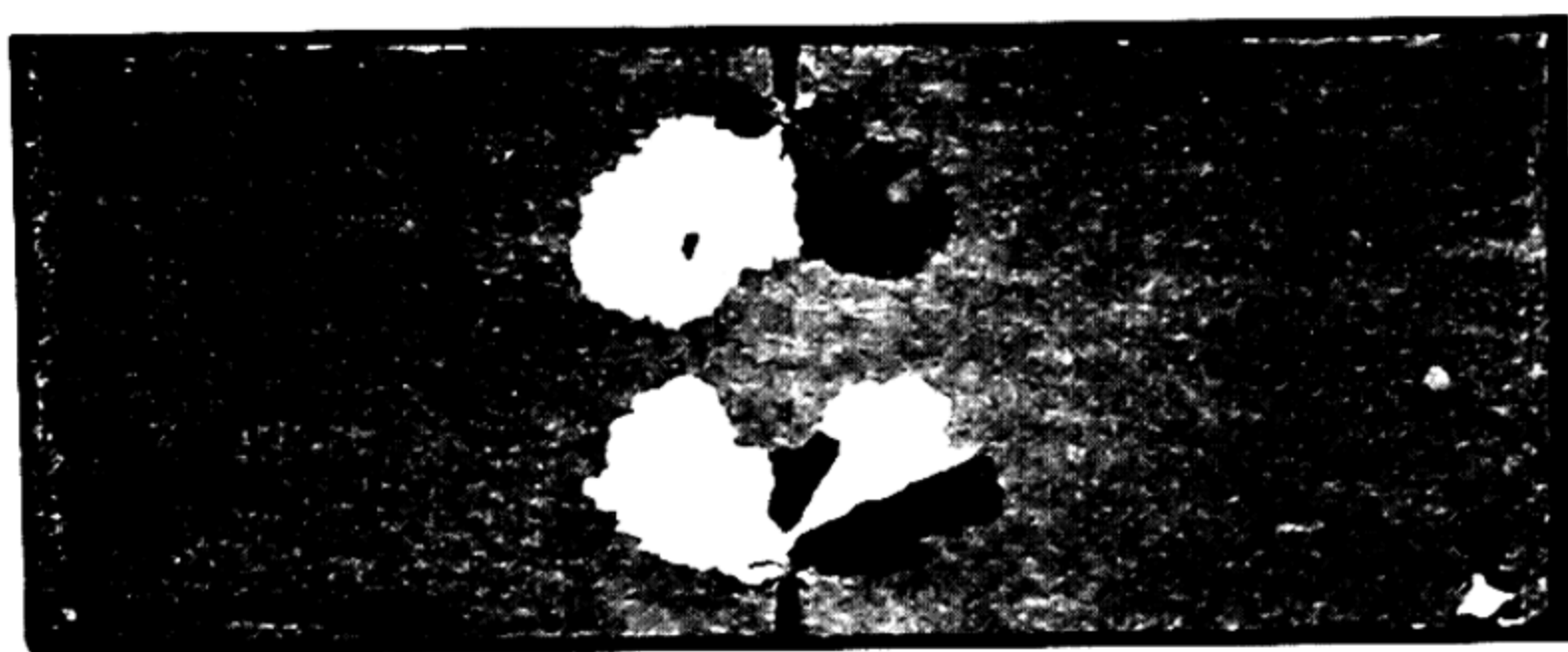


Figure 9. On recrystallization, nuclei are especially formed in regions of stress concentration.

a definite preferred orientation, which is composed of as many different "groups" as there are glide combinations which have taken part in the deformation process, whereby the mean orientation of each individual group can be deduced from that of the original single crystal by a rotation around an axis in the glide plane considered, perpendicular to the glide direction considered. (Compare figure 4).

This conclusion could actually be confirmed in a detailed investigation† of the recrystallization of homogeneously deformed aluminium single crystals. Before showing this to be the case, figure 10 may first be given as an experimental indication of the presence of a preferred orientation in general.

It also is due to van Arkel and shows an etched aluminium plate, figure 10 *b*, which had been rolled and thereafter recrystallized. Originally, figure 10 *a*, it consisted of a few large single crystals, the boundaries of which had been marked by ink lines. Although the recrystallized plate is entirely in a finely grained state, yet the regions originally occupied by the single crystals can still be clearly discriminated, thus showing that *in each region, the new crystallites occupy some*

* U. Dehlinger, *Metallw.* 12, 48 (1933); compare also H. G. Müller, "Zur Natur der Rekristallisationsvorgänge," *Physik. Z.* 35, 646 (1934).

† W. G. Burgers and P. C. Louwerse, *loc. cit.*; much more concisely in *Metallw.* 11, 251, 265 (1932).

preferred orientation, differing from that of the neighbouring crystals; this is what would be expected in connexion with the varying orientation of the original crystals, if in each of these crystals the mean orientation of the new crystallites is related in a definite way to the original orientation of the special crystal considered. The actual presence in a *homogeneously* deformed single crystal after recrystallisation, of a preferred orientation of the type mentioned above, may be clear from figures 11–13 (for details see the original papers).

They relate to the recrystallization of the disc, cut from a single crystal of aluminium, the Laue photograph of which in its undeformed state is shown in figure 3 *a*. From this photograph the positions of the cubic axes in relation to the plane of the disc were determined; they are represented by P_0 , Q_0 and R_0 in the stereographic projection figure 13 *b* (plane of projection parallel to plane of disc).

After careful compression (compare first footnote, page 141) up to 0.35 of its original thickness, the position of the lattice, as a consequence of rotations of the type

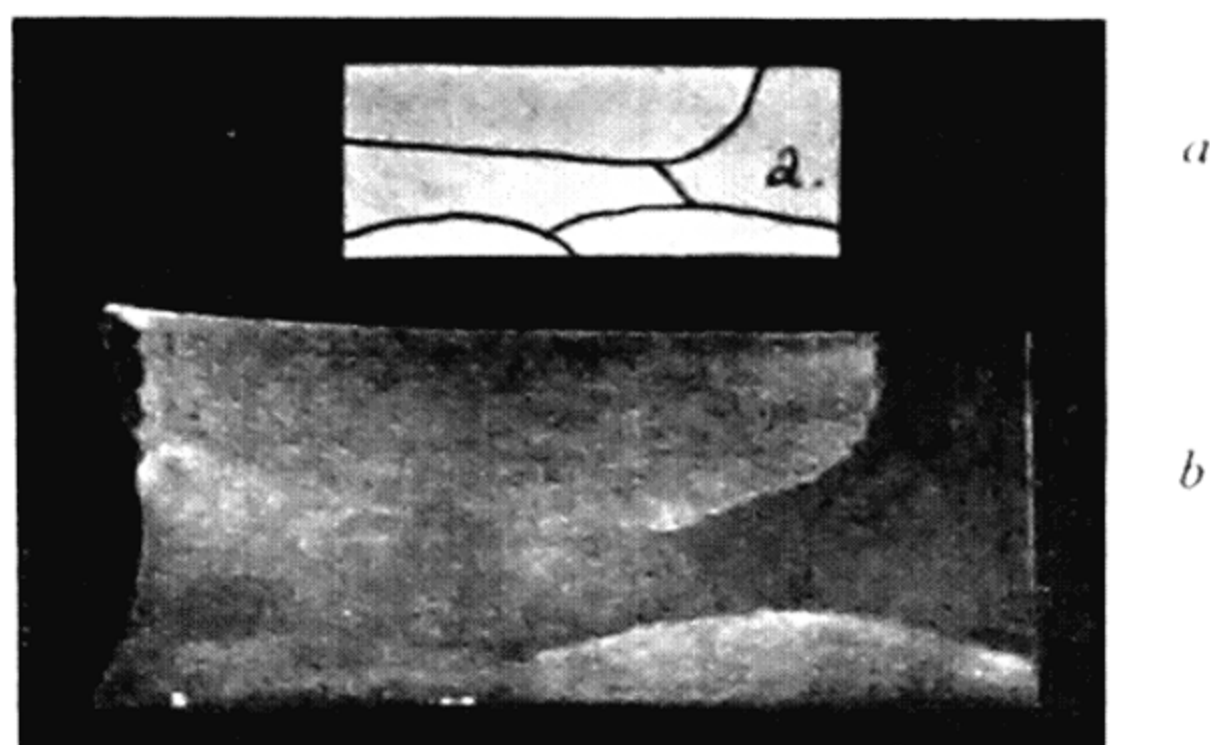


Figure 10. Recrystallization of a rolled aluminium plate, which originally (*a*) consisted of a few large crystals, the boundaries of which had been marked. In the recrystallized test-piece the regions, occupied originally by the single crystals, can still be discriminated (*b*).

represented in figure 1, had changed in such a way that (as was deduced from rotation photographs (compare figure 2)) it occupied the symmetrical “final position,” represented in figure 11, in which the direction of compression is parallel to a $[110]$ direction. In this position, which was already nearly reached after compressing up to $d/d_0 = 0.6$, the shear-stress conditions are equal for *four* glide combinations, viz. those operating along the octahedral planes $g(1)$ and $g(2)$ parallel to one or other of the two equivalent octahedral sides in each plane, for example *a* and *b* in plane $g(2)$. These four glide combinations can thus be expected to have taken part in the compression deformation (possibly to a different extent; see below) and to have given rise to “local curvatures” of the glide lamellae about four axes, lying in $g(1)$ and $g(2)$ perpendicular to the glide directions, the “sense” of these curvatures being as shown in figures 4 and 6. In figure 11 *two* of these axes, *c* and *d*, standing perpendicular to the glide directions *a* and *b* in the glide plane $g(2)$, are indicated, together with curved arrows, representing their “sense of rotation,” as will be clear from careful consideration of the figure.

As to the positions of the cubic axes (cube poles), the resulting lattice curvature is shown in stereographic projection in figure 12 (plane of projection again parallel

to plane of disc). Figure 12 *e* shows once more the "final position" of the elementary cube in the compressed disc before recrystallization, with *one* combination of glide plane g , glide direction G and "axis of curvature" A_{Kr} specially indicated. By means of the figures 12 *a* and 12 *b*, the stereographic projection, figure 12 *c*, will be understood; here P , Q and R represent the cube poles of the elementary cube in the compressed disc, while the three arrows indicate the positions occupied by P , Q and R if rotated about the axis of curvature A_{Kr} (compare figure 12 *b*), which stands perpendicular to the glide direction G in the glide plane g (the "ends" of the arrows correspond to a rotation of 50°). Thus

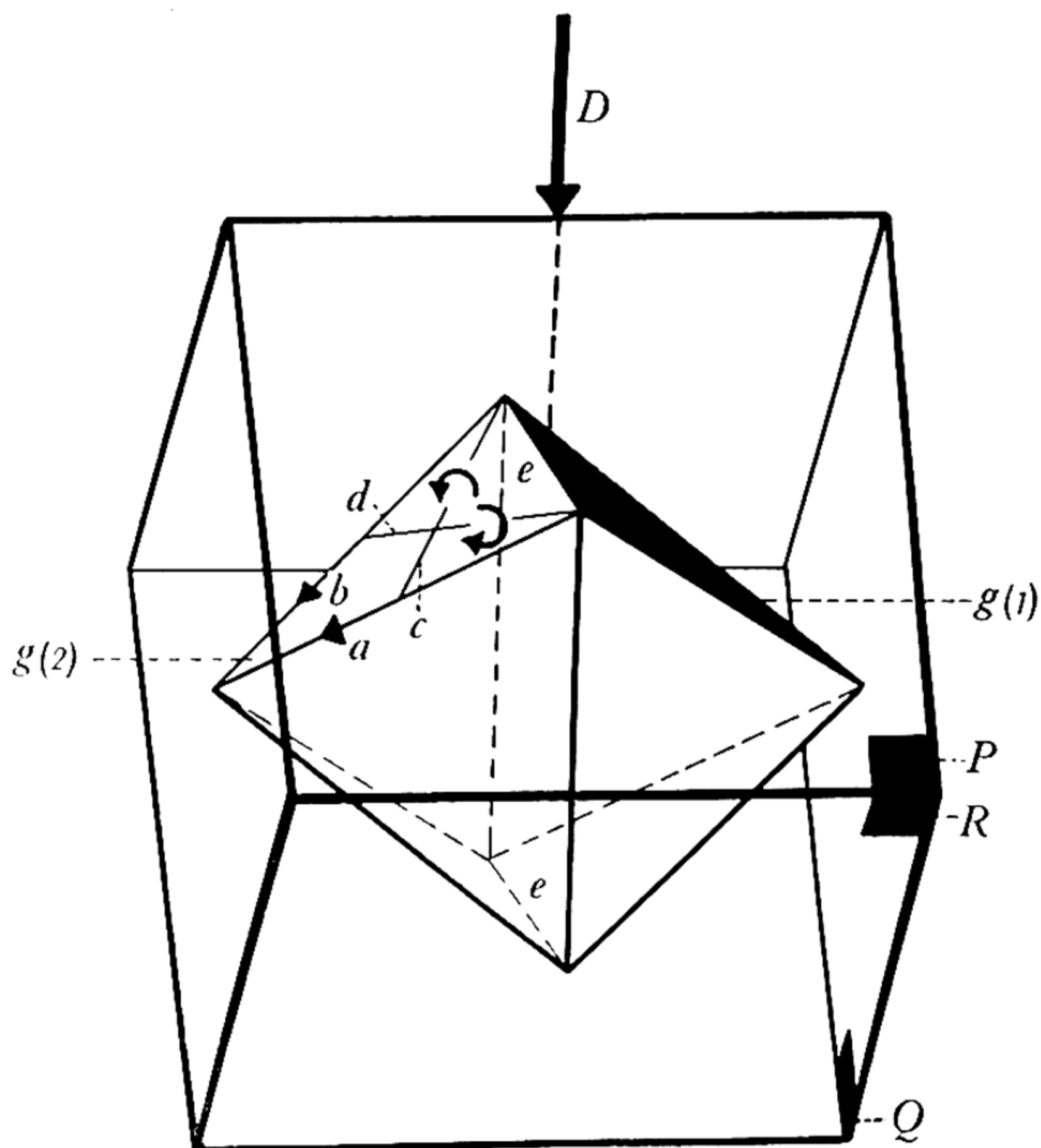


Figure 11. Final orientation of the lattice of an aluminium single crystal after continued compression: direction of pressure D parallel to a $[110]$ -direction.

the directions of these arrows indicate, for the glide combination considered, on the one hand the "local curvatures" of the glide lamellae in the compressed disc; on the other hand they must be expected to "fix" the cube poles of the corresponding group of crystallites formed on recrystallization, in case the supposition made previously regarding the formation of crystal nuclei is correct.

Finally figure 12 *d* has been obtained by completing figure 12 *c* with regard to the three remaining glide combinations which take part in the compression deformation of the single-crystal disc, as set forth in the discussion of figure 11. Figure 12 *d* thus shows four series of curves (each drawn differently), fixing the positions of the cube poles in the *four* groups of crystallites, which can be expected to occur in a strongly compressed single crystal disc on recrystallization.

The experimental results are summarized in figure 13. Figure 13 *a* shows a

10° oscillation photograph of the recrystallized disc (for this purpose it was heated at 600° C. during a few seconds only). By means of a complete series of such "oriented" oscillation photographs the positions of the cube poles in the recrystallized disc were completely determined. The result is shown in figure 13 *b* in stereographic projection, where the different shadowing of the cube-pole regions indicate their considerable variation in "density."

Now in the first place figure 13 *b* allows the conclusion that there are actually *four*

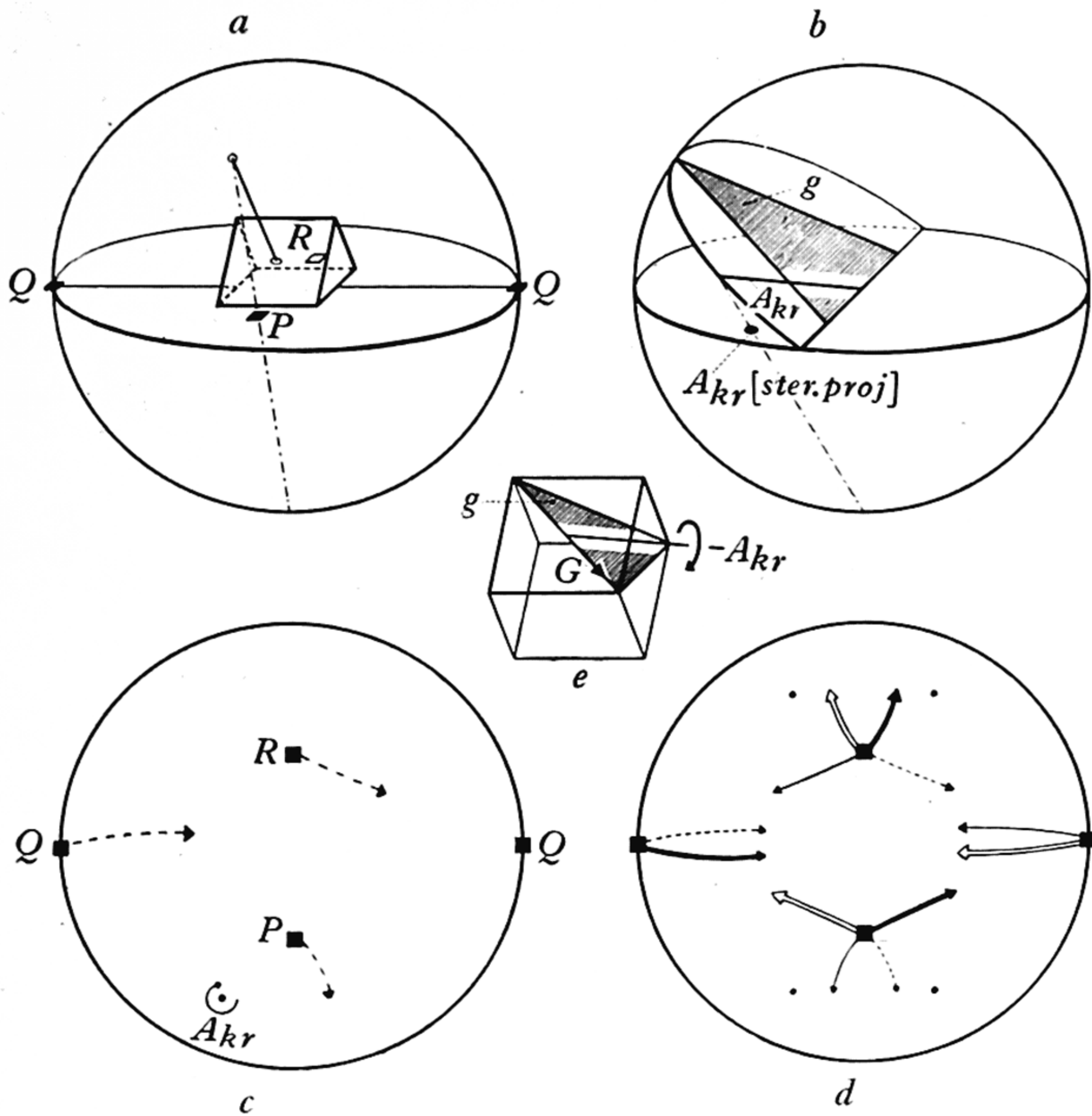


Figure 12. Representation (in stereographical projection of cube-poles) of the *fourfold* "local curvature" of glide lamellae in a severely compressed aluminium crystal about axes, which lie in the glide planes perpendicular to the glide directions (in *e* the relative position of *one* such axis A_{kr} , glide plane g and glide direction G is indicated separately).

differently oriented groups of crystallites in the recrystallized disc (each group being represented by *three* cube-pole regions at average distances of 90° from each other), in positions which are approximately fixed by the series of arrows of figure 12 *d**. The fact that the cube-pole regions show a considerable "dispersion" about the "theoretical" arrows is not surprising, as we may suppose that these

* The projection shows only *ten* cube-pole regions instead of twelve (= four times three). This is in consequence of the fact that figure 12 *d* contains two pairs of arrows (on the left and on the right of the figure), which are so close together that the corresponding pole regions overlap in the stereographic projection of figure 13 *b*.

latter represent only average directions of curvature of the original glide lamellae: deviations will occur as a consequence of local inhomogeneities in the crystal; moreover lattice regions where different glide lamellae "cross" each other may be "curved" about more than one axis. It can be further concluded from figure 13 *b* that the orientation of the newly formed crystallites differs from that of the mother crystal by rotations of 20 to 60° about the axes A_{kr} considered. This means that conditions are favourable for crystal growth only in the severely rotated regions of the local curvature, a fact which need not be surprising, as in these regions the relative dislocation of neighbouring atoms, and thus the stress-inhomogeneity, may be largest*.

The considerable variation in "density" of the cube-pole regions allows another conclusion to be drawn, which is of importance in connexion with what follows later (under (4)).

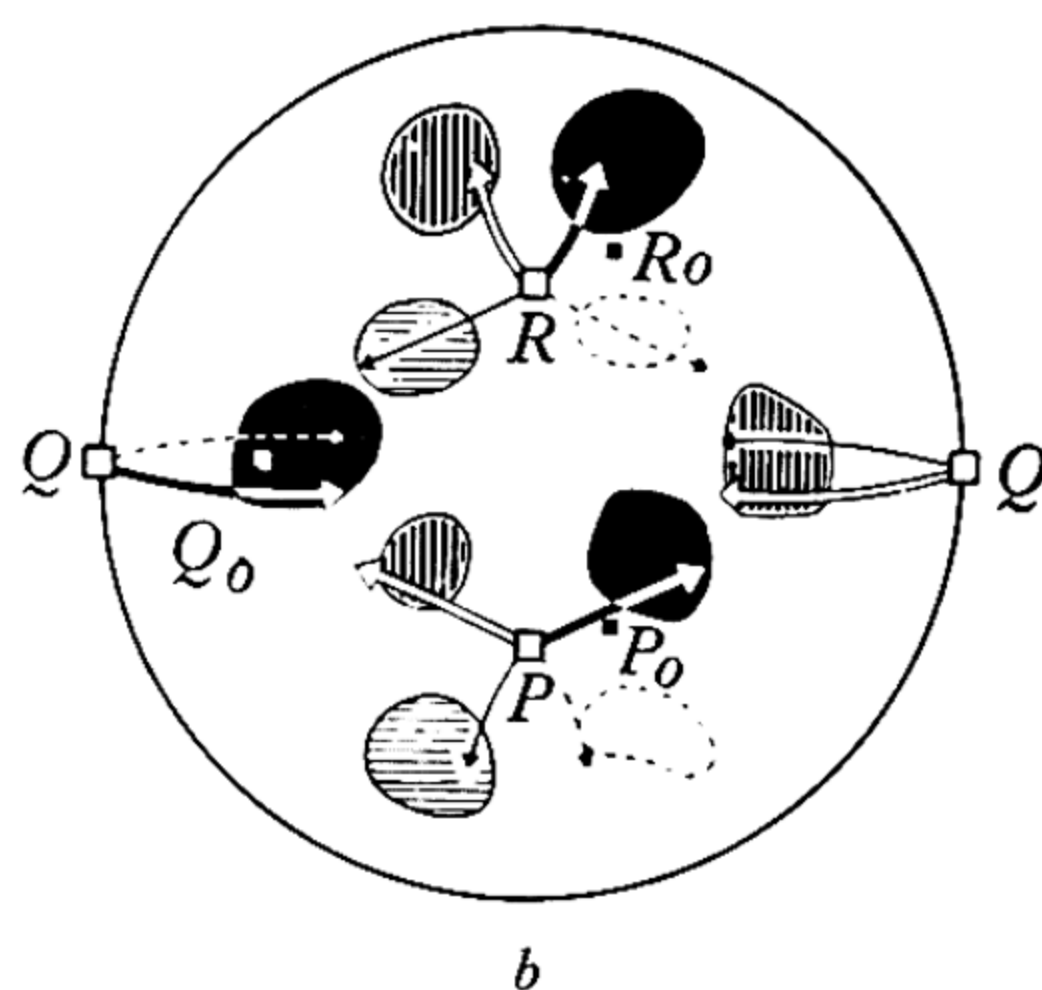
*a**b*

Figure 13. Recrystallization texture of a severely compressed aluminium single crystal disc after heating at 600° C. *a*, 10° oscillation-photograph, axis of oscillation in plane of disc (vertical in photograph); *b*, stereographic projection of cube-poles, and their relation to the position of the compressed crystal *before* heating: *four different groups of crystallites are present*.

From the analysis of the rotation and Laue photographs of the disc, taken after different stages of compression (and hence before recrystallization), the relative "activity" of the four glide combinations, which have brought about the change in the position of the crystal lattice from its starting position " $P_0-Q_0-R_0$ " (figure 13 *b*) into the final position " $P-Q-R$," could be deduced with great probability (for details see the original paper). It was found in this way that the glide combination corresponding to the thick arrows in figure 13 *b* (or 12 *d*) has been in operation from the beginning of the compression; then, after reaching a symmetrical position relative to the planes $g(1)$ and $g(2)$, the glide combination corresponding to the "double arrows" also took part in the deformation process; whereas only in the last stages of the compression, when approaching the "final position" represented in figure 11, did the two remaining glide combinations (thin and

* Compare W. G. Burgers and P. C. Louwerse, *Z. f. Phys. loc. cit.* p. 658.

dotted arrows in figure 13 *b*) come into a position, for which the shear-stress condition became equal to that of the combinations already active. From the fact, shown by figure 13 *b*, that the "density" of the cube-pole regions decreases in the same order as the "activity" of the glide combinations, it can be concluded that *for identical conditions of heating the chance to form an undeformed nucleus increases considerably with the amount of shear along a glide plane*, and thus (see under (2)) with the degree of bending of the "local curvatures."

Summing up, it can be said that *not only the individual glide processes which have taken part in the deformation but also their "relative activity" can to some extent be deduced from the recrystallization texture.*

On continued heating, a fine grained test-piece showing a definite recrystallization texture may be transformed into a few single crystals, *or even only one*, by subsequent growth of definite crystallites*. Investigation† of the orientation of these large crystals has shown that, in general, their positions do *not* lie within the "regions of maximal density" of the recrystallization texture, but somewhere outside or near the "boundary" of these regions. They thus correspond with nuclei which have been formed in "local curvatures" of the glide lamellae which either in "degree" or in "direction" of bending differ from the majority. This is of interest in connexion with the concept of Dehlinger‡ referred to above, according to which even in recrystallized grains there are still "residual" distortions and stresses. It is assumed that their "amount" differs in the various grains (probably according to the "state" of that special region of the deformed lattice where a definite grain is formed), and that this difference is the "driving force" for the subsequent growth.

(4) The above-indicated analysis of deformed and recrystallized aluminium single crystals by means of X-rays confirms the schematic conception of the "inner structure" of a "homogeneously" deformed crystal as shown in figures 5 and 6, especially as to the occurrence of "local curvatures" of glide lamellae.

Although in this conception of a plastically deformed crystal the "local curvatures" are fundamentally connected both with hardening and with recrystallization power, we should *not* expect a parallelism between these two properties, in the sense that for a given crystal a definite "shear hardening" corresponds with a definite recrystallisation power (this latter power being conveniently measured by the number of crystallites formed during a given heat-treatment§).

In fact, whereas it is the "total effect" of all these curvatures together, which is measured by the "hardness," it is the "distribution" of the energy surplus over the individual lattice distortion which determines the recrystallization power. This was clearly demonstrated by the analysis of the recrystallization texture of figure 13 *b*, where it was found that for definite conditions of heating, the chance of forming an undeformed nucleus increases with the amount of shear and thus with the degree of bending of a local curvature.

It is therefore clear that we may expect a *difference in recrystallization power between two crystals which have undergone the same shear hardening*, in one case (compare figures 6 *b* and 7 *a*) by shear along *one* glide plane, in the other case

* A. E. van Arkel and M. G. van Bruggen, *Z. f. Phys.* 51, 520 (1928).

† W. G. Burgers and J. C. M. Basart, *ibid.* 54, 74 (1929).

‡ U. Dehlinger, *Metallw.* 12, 48 (1933).

§ It is here supposed that this number corresponds to that of the nuclei formed.

(figures 6 *c* and 7 *b*) by shear along *more than one* glide plane: in the sense that the number of nuclei will be *greater*, the *less* the number of glide planes which have taken part in the deformation process, since in this case the average bending of the "curvatures," and thus their stress content, is larger.

This is now confirmed by experiments*, as the following examples may show.

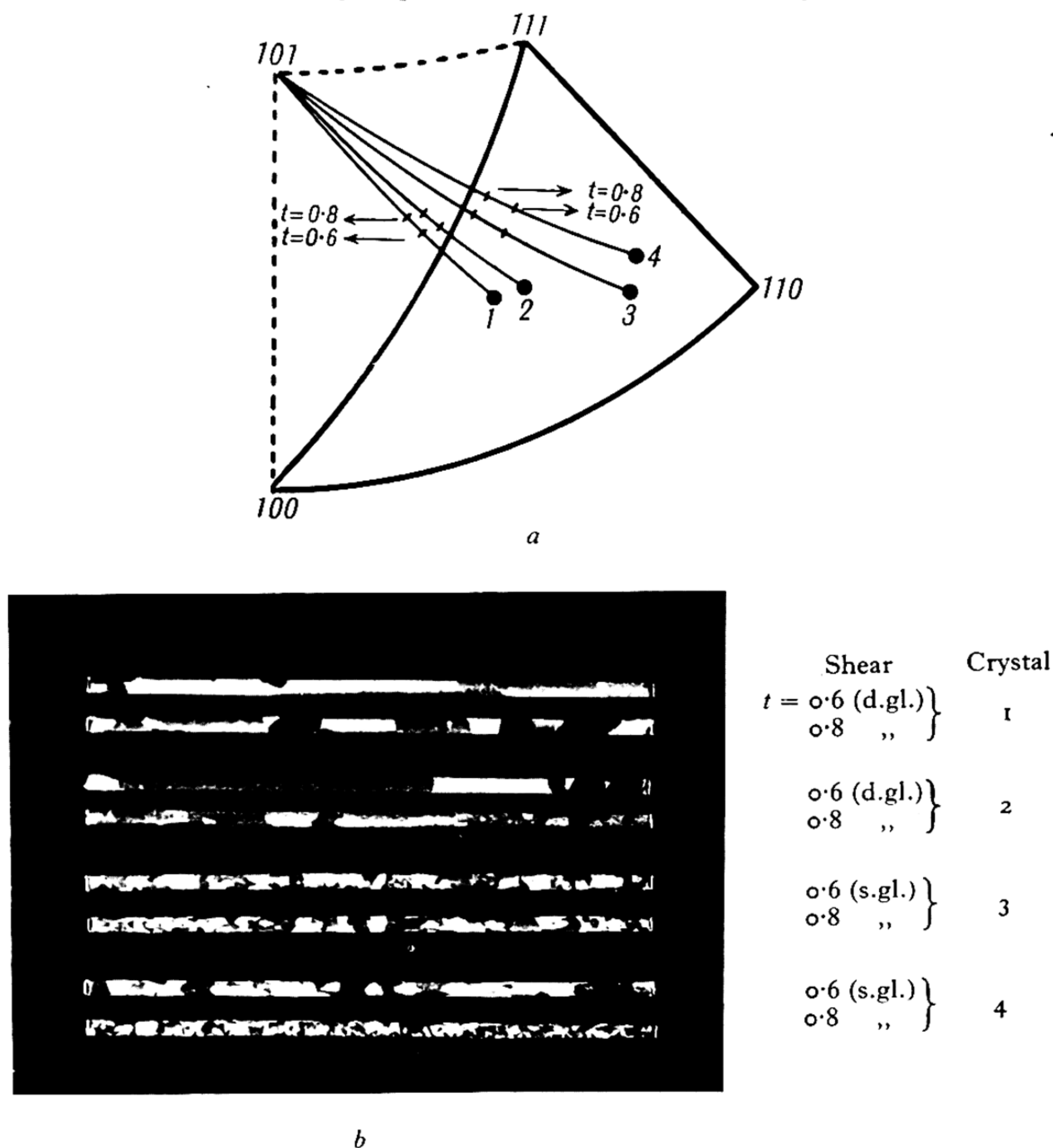


Figure 14. Difference in recrystallization power between crystals which have undergone "double gliding" (Nos. 1 and 2) and "single gliding" (Nos. 3 and 4): the number of crystals, formed for the same *total* shear t , is less in the former than in the latter: *a*, "theoretical" change in position of the lattice relative to the direction of stretching for shears $t = 0.6$ or 0.8 ; *b*, recrystallized test-pieces.

Figure 14 relates to four aluminium single crystal rods, the directions of the axes of which are shown in stereographic projection. Of each crystal two pieces have been stretched so far as to correspond to shears of 0.6 and 0.8 respectively†. As is clear from the stereographic projection (figure 14 *a*), the orientation of crystals

* W. G. Burgers and J. J. A. Ploos van Amstel, *Z. f. Phys.* **81**, 43 (1933); *Nature*, **131**, 326 (1933).

† The amount of stretching required for a definite shear can be determined for an arbitrary crystal orientation with the aid of diagrams, given in Frhr. v. Göler and G. Sachs' paper (*Z. f. Phys.* **41**, 103 (1927)).

3 and 4 was such that for both degrees of stretching, gliding took place along one glide plane only (but for the occurrence of "forbidden glidings"), whereas for crystals 1 and 2 the symmetry line $[100]$ – $[111]$ between two "fundamental triangles" $[100]$ – $[110]$ – $[111]$ and $[100]$ – $[101]$ – $[111]$ has been passed, so that "double gliding" might be expected to have occurred in these cases*. On recrystallizing the stretched rods at 600° for 15 min., the number of crystals (figure 14 *b*) formed in these last rods, in which double gliding has taken place, is much less than in rods 3 and 4, where only one set of glide planes has taken part in the deformation process, in accordance with the view set forth above.

The same effect can be shown in a much more striking way by the following experiment. It is a well-known fact that on stretching an aluminium single crystal, not only the "theoretical" glide plane for which the component of shear stress is maximal, but also so-called "forbidden glidings" take part in the glide process to a greater or lesser extent. If we assume the probability of gliding in a definite glide plane to be proportional to the shear stress along this plane, we may predict for what direction of stretching the probability of the occurrence of multiple gliding is largest and smallest respectively, by calculating† the *average* of the shear stresses along all twelve possible glide combinations for different directions of stretching. As this quantity, expressed in terms of the applied tensile stress as unity, varies from 0.27 for the $[100]$ direction to 0.14 for the $[110]$ and $[111]$ directions, we find that the probability of multiple gliding is largest for the $[100]$ direction (for this direction the ratio $\frac{\text{shear stress}}{\text{tensile stress}}$ has a *high* value (0.41) for eight of the twelve possible glide combinations) and smallest for the $[110]$ and $[111]$ directions.

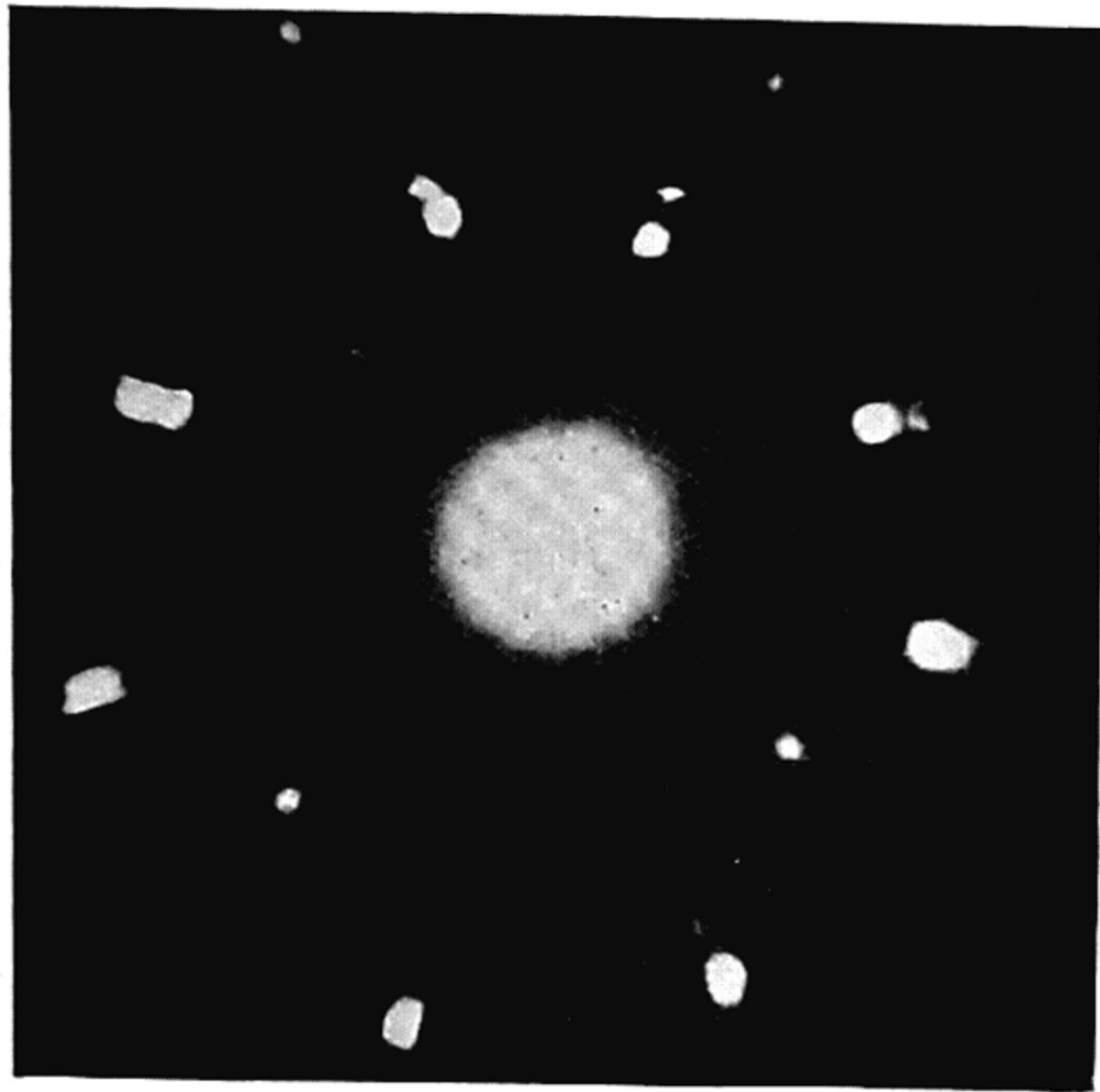
We may thus expect a difference in recrystallization power for aluminium crystals of varying orientation, stretched over the same total shear, in the sense that the number of crystallites formed on heating will be larger, the nearer the crystal axis lies to the line $[110]$ – $[111]$. This is confirmed by figure 15 *b*, where five crystal rods are shown, the orientations of the axes of which are again represented in stereographic projection in figure 15 *a*.

The maximal difference in recrystallization power may be expected to exist for aluminium crystals stretched along $[100]$ and along $[110]$, in the sense that the former gives rise to the formation of a smaller number of crystals than the latter. This is now confirmed by experiment in a striking way, as is clear from figure 16, which shows four pieces of an aluminium single crystal, *two* (figure 16 *a'*) with the length direction parallel to $[100]$ and *two* (figure 16 *b'*) with their direction parallel to $[110]$. On stretching all these crystal pieces 10 per cent, that is, as calculation shows, practically to the same total amount of shear, their hardening proved to be practically the same; Laue photographs showed, however, that the spots (figure 16 *a*) of the crystal stretched parallel to $[100]$ have practically remained unaltered, whereas those (figure 16 *b*) of the crystal stretched parallel to $[110]$ have been elongated, thus

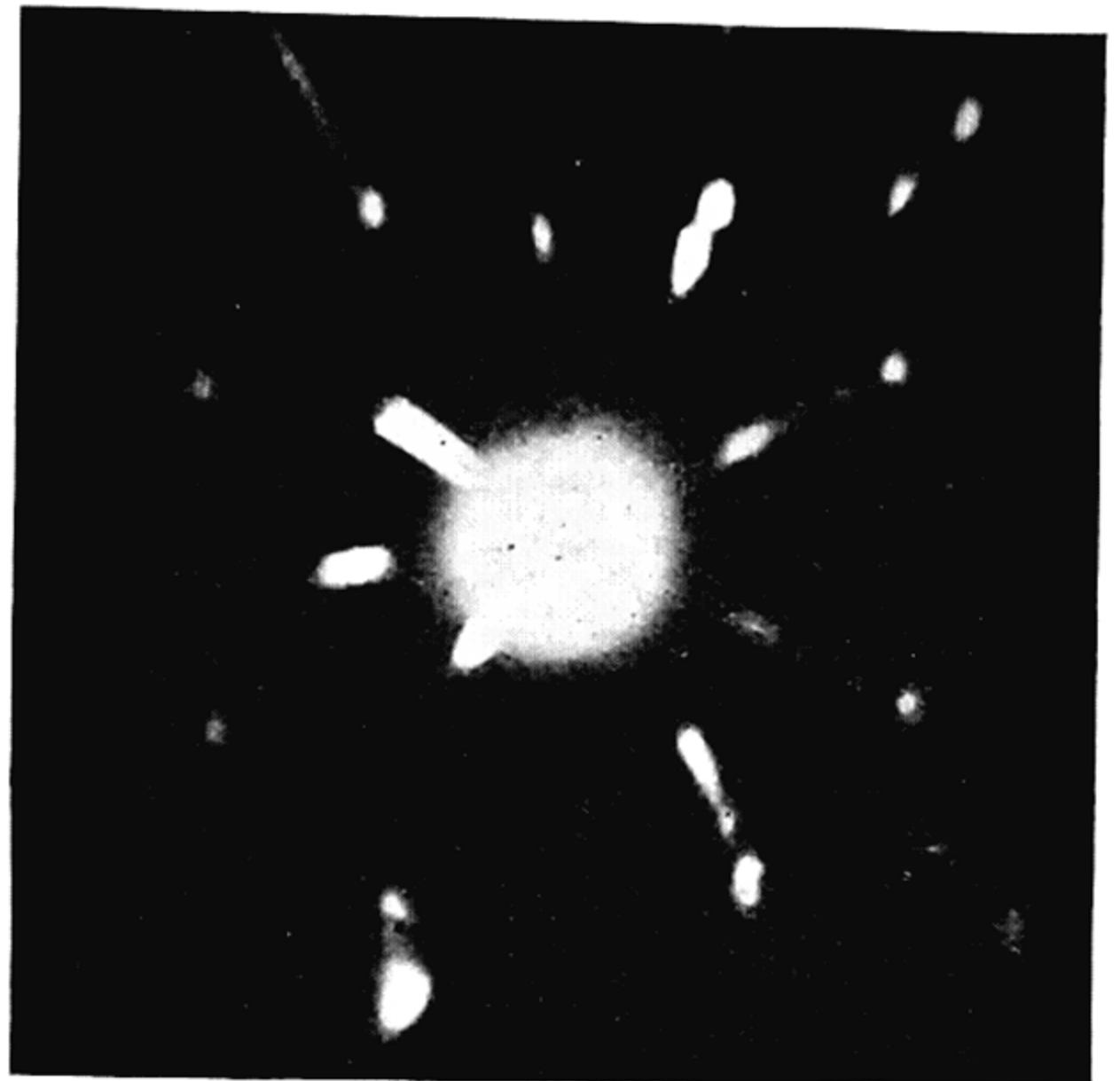
* G. I. Taylor and C. F. Elam, *Proc. Roy. Soc. A*, 108, 28 (1925); Frhr. v. Göler and G. Sachs, *Z. f. Phys.* 41, 103 (1927).

† Compare W. Boas and E. Schmid, *Z. f. techn. Phys.* 12, 71 (1931).

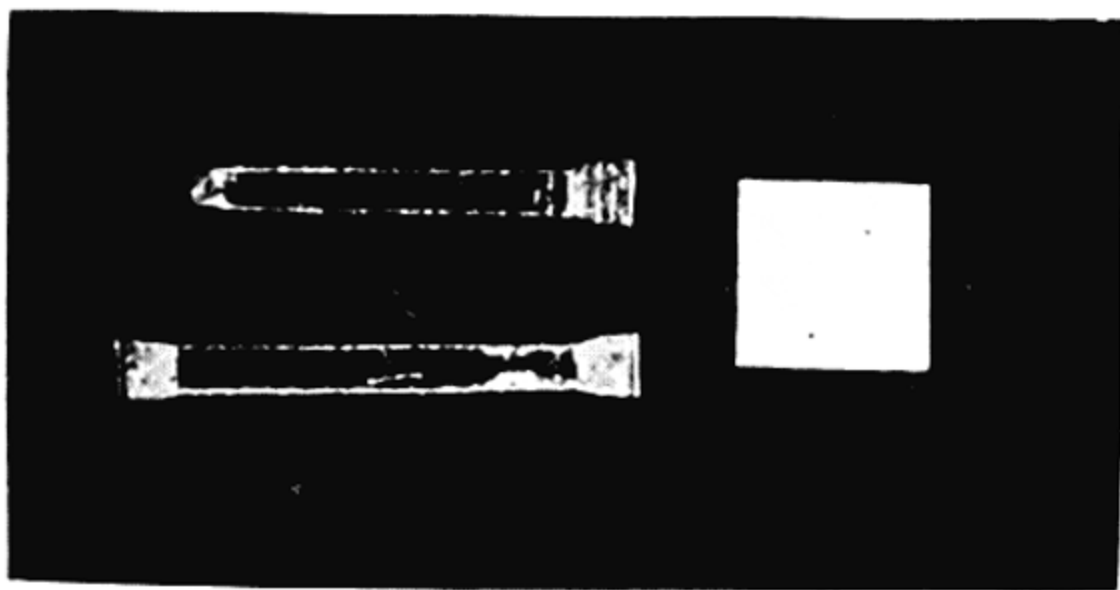
(5) Thus we finally come to the conclusion that a definite shear hardening may be connected with different states of lattice distortions, i.e. schematically speaking, the "co-operation" of a large number of "weak" curvatures or a small number of "strong" curvatures. The recrystallization power is attributed to the "distribution" of stress content over the individual curvatures; it is thus conceivable that the first state gives rise to the formation of a smaller number of crystallites than the latter state.



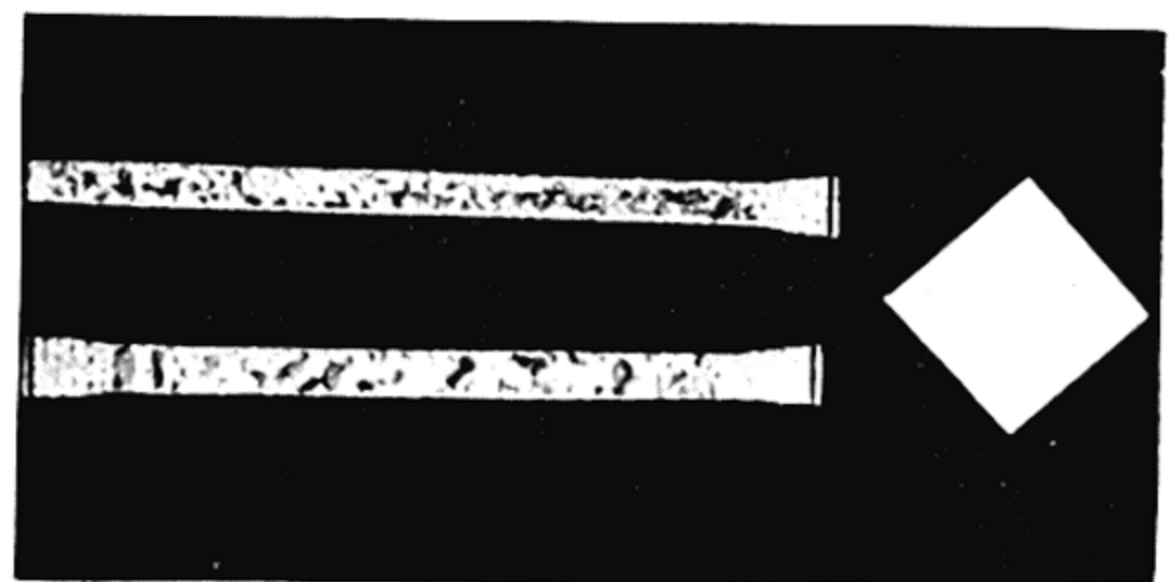
a



b



a'



b'

Figure 16. Difference in distortion and in recrystallization power on stretching an aluminium single crystal to *practically the same shear hardening*: *a, a'*, (nearly) parallel to a $[100]$ -direction; *b, b'*, (nearly) parallel to a $[110]$ -direction.

If now we stretch a test-piece consisting of a number of differently oriented crystals, we may expect that the recrystallization power of the individual crystals will be different, as some have undergone "simple" and others "complicated" shear, thus giving rise to different systems of "lattice curvatures" within them. That this expectation comes true is clearly shown* by figures 17, 18: the three crystallites I, II and III, marked in figure 17 *a*, after stretching the whole test-piece about 10 per cent, gave rise to the Laue photographs in figure 18 *a, b* and *c* respectively. After heating the test-piece at 600° (figure 17 *b*) several new crystallites

* W. G. Burgers, *Metallw.* 11, 265 (1932).

were formed in II, and *none* in I, in accordance with the fact that the Laue spots in photographs 18 *a*, *b* indicate the presence of "stronger curvatures" (corresponding to a "simpler" glide process) in II than in I (III represents an intermediate state).

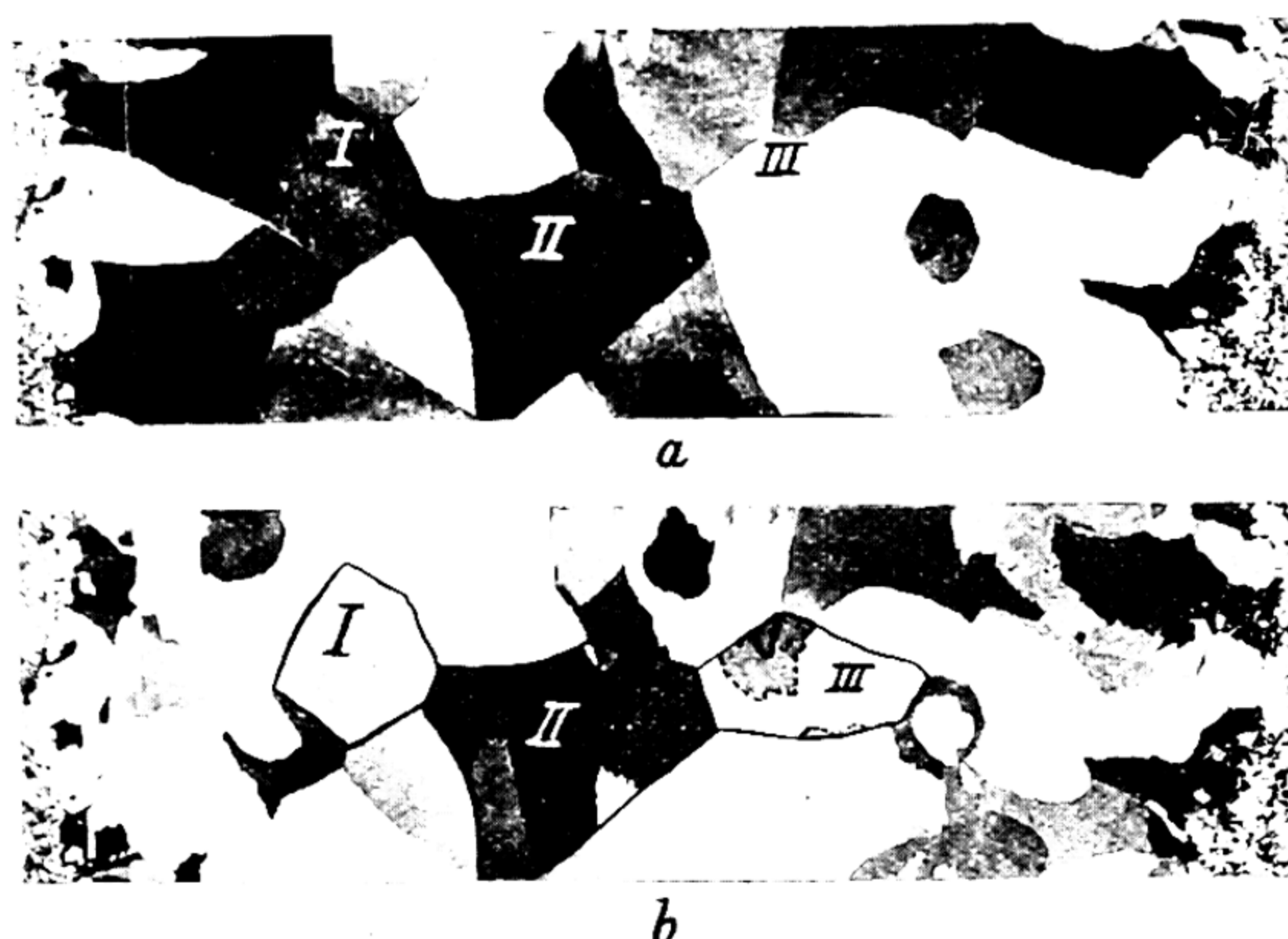


Figure 17. Difference in recrystallization power between *various* crystals of a polycrystalline test-piece: *a*, original state; *b*, after 10 per cent stretching and subsequent heating at 600° C.: the number of crystallites formed in the crystals I, II and III is quite different (none in I, several in II, a few in III).

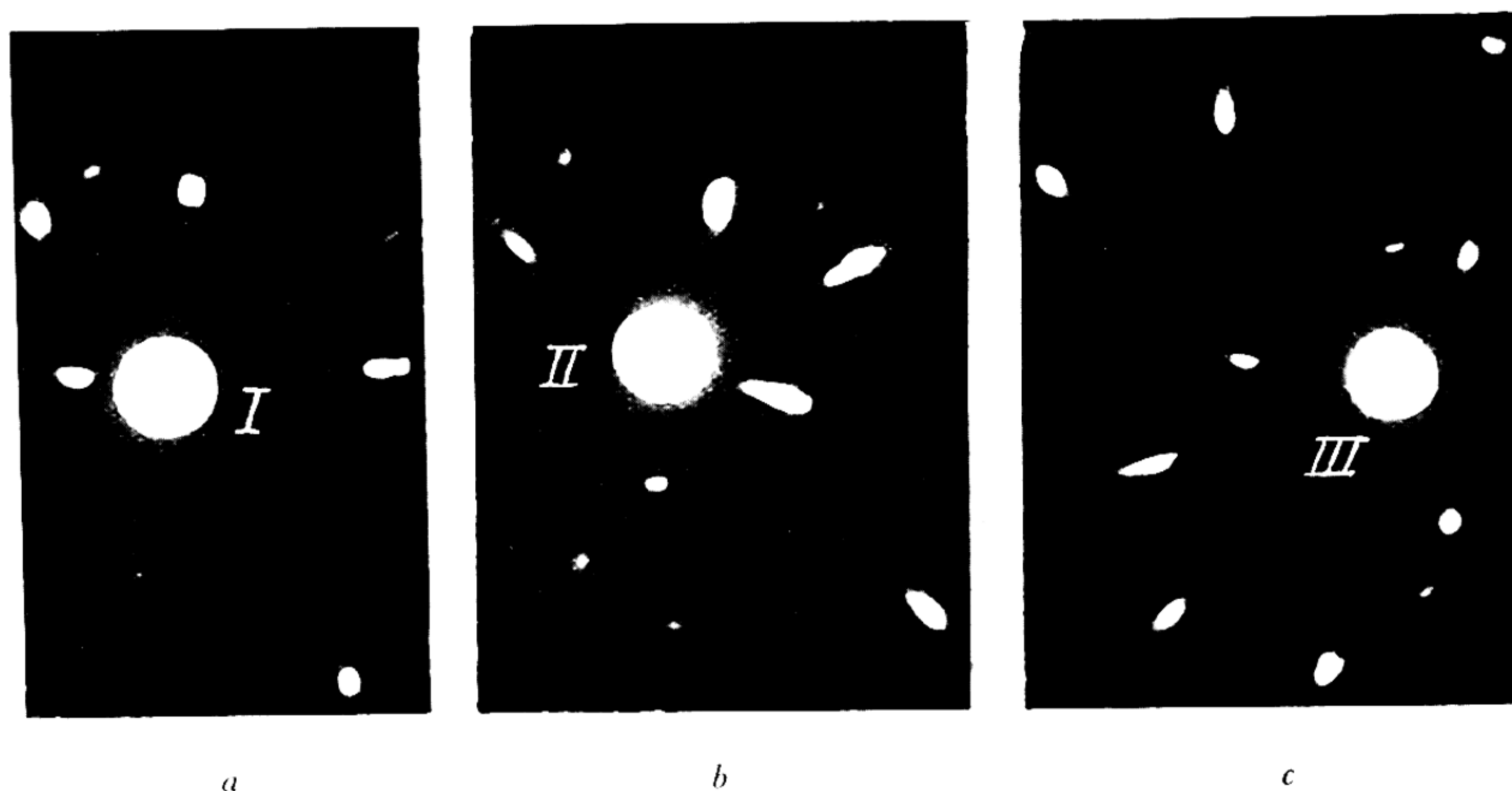


Figure 18. Laue photographs of crystals I, II and III in the *stretched* aluminium plate of figure 17 *a* before recrystallization.

This difference in recrystallization power of the individual crystallites of a polycrystalline test-piece, in connexion with the extreme recrystallization power of crystals stretched along [110], seems to us to give an explanation of the experimental fact, observed by several investigators*, that large aluminium crystals, grown by recrystallization of strained

* C. F. Elam, *Phil. Mag.* 50, 517 (1925); E. Schiebold and G. Sachs, *Z. f. Krist.* 63, 34 (1926). For further references see note *, p. 152.

polycrystalline test-pieces, seem to favour a position in which a $[110]$ direction is parallel to the direction of stretching: it seems probable that, on stretching a polycrystalline aggregate, a crystal grain of this special orientation will exhibit an extreme recrystallization power and serve as nucleus for the single crystal formed on heating.

The above may perhaps help us to understand the experiments of van Arkel and van Bruggen*, who found that aluminium test-pieces of rather variable crystal size, after stretching to the same load per mm^2 , on heating give rise to the formation of an equal number of crystallites: their test-pieces consisted in all cases of a fairly large number of crystallites, so that in a given test-piece crystallites were present which, if we neglect the influence of the glide distortion at their boundaries, had undergone simple, as well as others which had undergone complicated shear; thus the number of crystallites formed on heating was probably the average for all crystal orientations for the given shear applied †, and the differences observed by us for single crystals need not occur in their experiments. It is, however, difficult to discuss these experiments in detail, as, of course, the hardening caused by the glide distortions at the boundaries of the crystallites plays an important part in this case.

That, however, the parallelism between hardening and recrystallization power, as shown in this case, is more accidental than fundamental and due to the special conditions of the experiment, is clear from experiments with crystals under flexural and torsional stress, as have been performed by Czochralski, Sachs, Beck and Polanyi, and van Arkel and van Bruggen. For details we must refer to the original papers ‡. Here only one experiment may be mentioned, described by Beck and Polanyi§, which clearly demonstrates the fundamental *non*-parallelism between the two properties mentioned. An aluminium single-crystal rod was bent through a certain angle and then restraightened over half its length. Ball-hardness tests showed that the restraightened part was "harder" than the bent part; on recrystallization, however, crystallites grew in this latter "weaker" part, whereas they were not formed in the "harder" straight part of the crystal rod.

In connexion with the foregoing, we may say that regarding the "distribution" of stress concentration, the bent and the restraightened part of the crystal rod can be discriminated by such schematic figures as those given in figures 7 *a* and 7 *b* respectively. Thus we attribute the decrease of recrystallization power on restraightening, in agreement with Polanyi, to a decrease of stress content in the "curvatures" formed during the foregoing bending, whereby the increase of the hardening can be accounted for by the formation of new ("small") curvatures (and consequent lattice distortions) as a result of the working of other glide planes on restraightening||.

* A. E. van Arkel and M. G. van Bruggen, *Z. f. Phys.* 42, 795 (1927).

† On account of the high degree of symmetry of aluminium, a given stretch corresponds approximately to a given *total* shear for all crystal orientations: see v. Göler and Sachs, *loc. cit.*

‡ See for references, and for a more detailed discussion of these experiments, W. G. Burgers, *Z. f. Phys.* 81, 43 (1933).

§ P. Beck and M. Polanyi, *Naturwiss.* 19, 505 (1931); *Z. f. Elektroch.* 37, 521 (1931).

|| On further bending in the same direction, the average curvature can increase again and with it the recrystallization power: compare A. E. van Arkel and M. G. van Bruggen, *Z. f. Phys.* 80, 804 (1933) for analogous experiments with crystals under torsional stress.

APPENDIX*

(6) “*Transformation-hardening.*” Before concluding this paper, a few words may be added regarding a type of recrystallization process, which is essentially different from that considered so far. It occurs, at least in several cases (carbon-steel, brass, cobalt, zirconium), on transition of one phase (modification) of a metal or alloy into

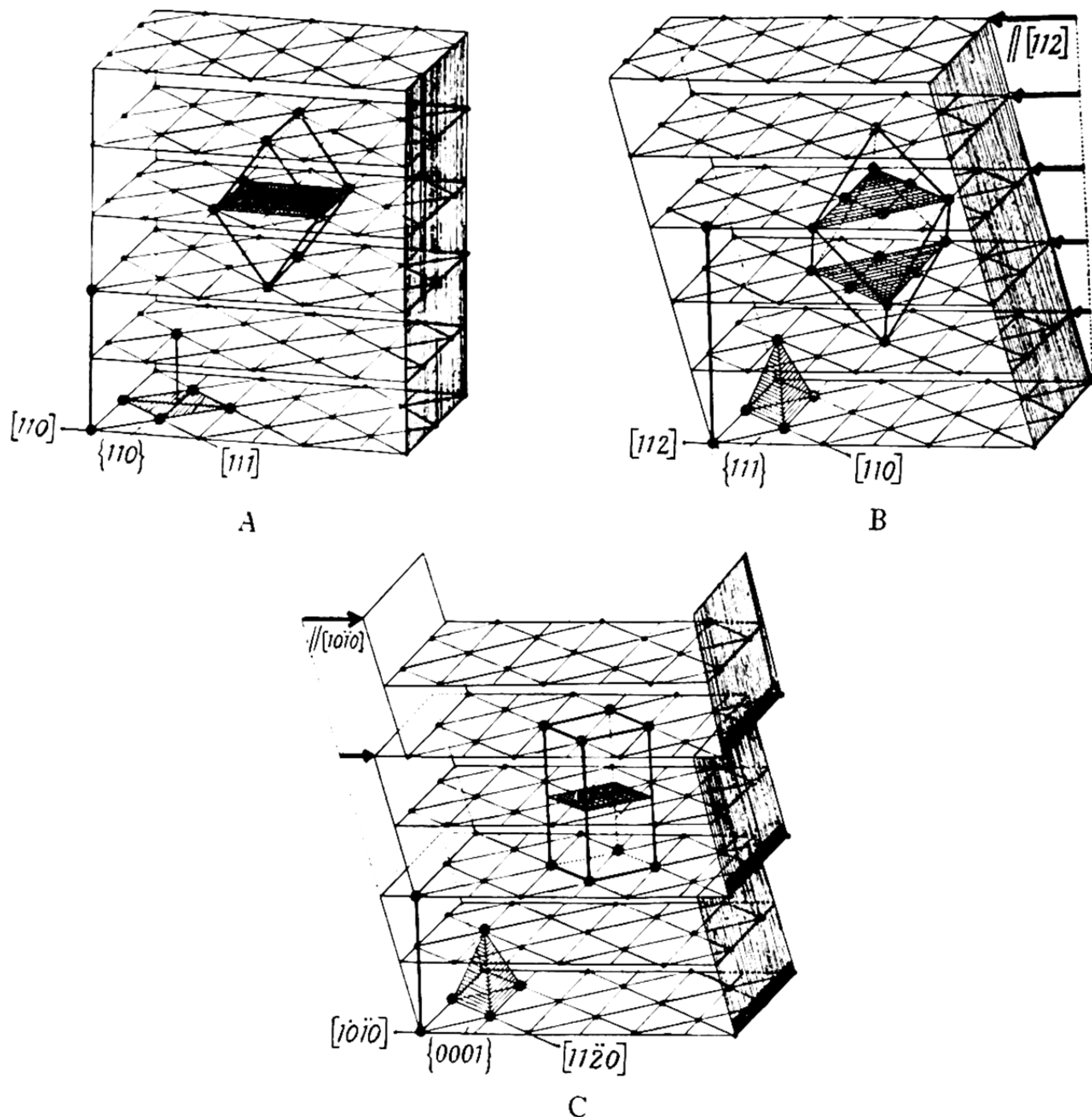


Figure 19. Schematic illustration of the shearing operations, which can transform a body-centred lattice A, via an intermediate face-centred lattice B, into a lattice with atoms in positions corresponding to those of the hexagonal close-packed lattice C†.

another, and can be described as a homogeneous deformation of the initial crystal lattice, consisting of one or more simple shears parallel to definite crystallographic

* See for references concerning a large number of papers by several investigators, dealing with the questions raised in this appendix, W. G. Burgers and F. M. Jacobs, “On the process of transition of the cubic body-centred modification into the hexagonal close-packed modification of zirconium,” *Physica*, 1, 561 (1934).

† The actual transformation of a *cubic* body-centred lattice via a *cubic* face-centred lattice into a truly *hexagonal* close-packed lattice requires an additional shear operation, together with special dilations and contractions of the lattice, which are not illustrated by figure 19.

planes and directions, combined with (in general small) dilatations or contractions. Figure 19 may serve as an illustration: it shows the way in which for example a sequence of two shear operations may transform a definite body-centred lattice A via an intermediate face-centred lattice B into a lattice C with atoms in similar positions to those occurring in the hexagonal close-packed lattice; the shear plane corresponding in the various lattices to a $\{110\}$, a $\{111\}$ and a $\{0001\}$ plane respectively*.

It is clear that the shear operations lead to the existence of a definite crystallographic relation between the orientation of the crystals of the newly formed phase and those of the original phase. Thus, for example, a single crystal of the cubic body-centred modification of zirconium, while passing over into the hexagonal close-packed modification at about 870°C. , gives rise to a limited number (maximally 12) of orientations of the hexagonal lattice; these being such that in each of them the $\{0001\}$ plane and a $[11\bar{2}0]$ direction are parallel respectively to a $\{110\}$ plane and a $[111]$ direction of the cubic lattice. It is actually from the existence of such a crystallographic relation that the "mechanism" of the process can be deduced, at least to some extent.

In some cases, however, an experimental indication of the occurrence of a "homogeneous" process is obtained, if, after transition of an α phase into a β phase and back again, the *original* orientation of the α crystal is obtained again: this will occur if the same shear plane (s) and direction (s) have been active in both transition processes. An example of this is shown in figure 20, which again relates to the transition of cubic into hexagonal zirconium and *vice versa*.

In connexion with the subject of the present paper, it is, moreover, of interest to point to a characteristic feature of such a "homogeneous" transition process, viz. that smaller or larger regions of the original crystal lattice are "coherent" with regard to the transition, so that nowhere within them are the initial and the final states of the metal simultaneously present.

This may lead to a remarkable difference between this process and that occurring on recrystallization of a strained metal with regard to their *influence on the hardness* (and eventually other physical properties, as electrical resistance, magnetic hardness) of the metal. Whereas in a strained test-piece the growth of nuclei (see figure 8) gives rise to the formation of practically stress-free crystallites†, and thus to an "annealing" of the test-piece, *the transformation process, on the contrary, may cause it to become harder.*

In fact, as a consequence of the presence of different "equivalent" shear planes in a crystal lattice, or (in the case of a polycrystalline test-piece) of differently oriented crystallites, the directions of the transformation shears and contractions (or dilatations) need not be the same in the whole test-piece. It is, therefore, conceivable that internal stresses and distortions may be created by "shear interference" between neighbouring lattice regions, which themselves are coherent with regard to the transformation.

* See p. 158, footnote †.

† Compare however p. 151 (small print).

Such an effect may give rise to a "hardening" of the test-piece: it was actually observed in a rod consisting of zirconium crystals, if by rapid cooling the transition point was passed as quickly as possible, in order to prevent release of tension of the

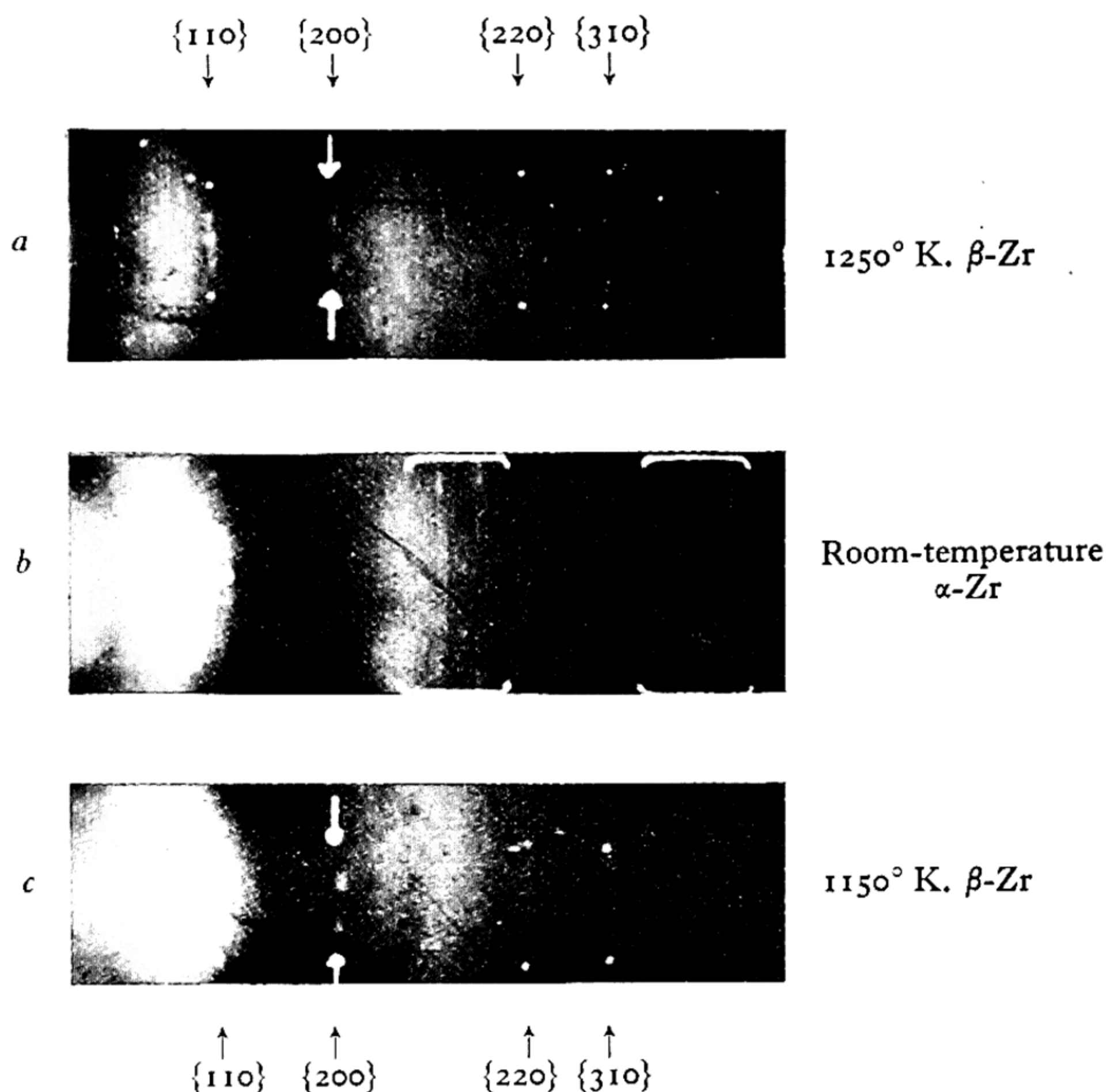


Figure 20. X-ray rotation photographs* of a definite part of a zirconium wire at different temperatures. Photographs *a* and *c* show practically the same arrangement of spots (see especially the identical positions of the (200)-reflections); in this case, therefore, a cubic β -crystallite regains its original orientation after the transition of the hexagonal α -phase (photograph *b*) and back again.

* Unfortunately these photographs have been damaged rather badly by scratches. Moreover they show a strong diffuse scattering, due to the Lindemann glass surrounding the wire.

stresses introduced by the transformation process. By heating such "hardened" crystals at a temperature not too much below the transition point, they can be made weak. An analogous behaviour was observed by Wassermann† in nickel-iron wires, which were subjected to repeated transitions from the cubic face-centred into the cubic body-centred phase.

† G. Wassermann, *Arch. f. das Eisenhüttenw.* 6, 347 (1933).

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ON PLASTICITY, CRYSTALLOGRAPHIC AND NON-CRYSTALLOGRAPHIC

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ABSTRACT. The paper is largely devoted to summarizing experimental data on crystal plasticity. It is pointed out that with regard to elasticity, Cauchy's relations are in general obeyed by ionic, but not by metallic, crystals.

The behaviour of crystals with regard to plasticity is then considered, first with reference to slip and then to mechanical twinning. As regards the former, which is marked particularly by the fact that it occurs in directions and along planes which are definitely marked out in the crystal lattice, it is pointed out that yielding shows an abrupt onset, and commences at a definite critical shear stress. This quantity is tabulated for a number of crystals, and its temperature variation shown graphically. It is pointed out that, just as the yield point can be expressed by this single constant, so the stress-strain curve can be expressed in a single curve, the hardening curve. In this, the shear strength of the slip system concerned is plotted as a function of the shear. This curve gives at once the hardening due to any degree of shear.

As regards twinning, the available knowledge is less quantitative. The effect of temperature on it is less marked than on slip, and like the latter process, it leads to strengthening of the crystal.

The final section of the paper deals with those types of plasticity which show no definite relation to the net-planes of the lattice. Among these processes are creep and a remarkable plasticity during phase-change of specimens under load.

IN the theory of the solid state, the investigations which would be expected to give in the most direct manner a measure of lattice forces, namely those on the strength of crystals, still present a difficult problem. The object of this paper will be to bring forward in a very condensed form some experimental data on crystal deformation, at a conference where help in the explanation of the results may confidently be expected.

1. THE ELASTICITY OF CRYSTALS; CAUCHY'S RELATIONS

Even in the elastic deformation of metals a remarkable divergence from theory is encountered, which was noticed very early^(1, 2). The equations expressing the generalized Hooke's law for triclinic crystals involve 21 constants. This number is reduced to 15 if no account is taken of the interaction between the component simple lattices. That is, six new relations are obtained, identical with those obtained by Cauchy in 1828. These six equations are: $c_{23} = c_{41}$, $c_{56} = c_{14}$, $c_{64} = c_{25}$, $c_{31} = c_{55}$, $c_{12} = c_{66}$ and $c_{45} = c_{36}$ *. According to Born's theory, these relations

* c_{ik} and s_{ik} are elastic constants (Voigt's notation).

should be valid if each element of the crystal is a centre of symmetry. Since this latter property cannot be destroyed by elastic displacements, mutual interaction of the component lattices is already excluded by the assumed structure of the crystal. Table 1 gives the values of the elastic constants of several materials. It will be seen

Table 1. Validity of the Cauchy relations

$$c_{12} = c_{44} \text{ valid}$$

Crystal	c_{12} 10^{11} Dyn./cm ²	c_{44} 10^{11} Dyn./cm ²
NaCl	1.37	1.28
NaBr	1.31	1.33
KCl	0.64	0.65
KBr	0.58	0.62
KI	0.43	0.42
Cu	12.3	7.52
Ag	8.97	4.36
Au	15.7	4.36
Al	6.22	2.84
α -Fe	14.1	11.6
W	19.8	15.1

$$c_{12} = c_{44} \text{ not valid}$$

Crystal	c_{12} 10^{11} Dyn./cm ²	c_{44} 10^{11} Dyn./cm ²
CaF ₂	4.48	3.38
NaClO ₃	- 2.10	1.20
FeS ₂ (Pyrites)	- 4.74	10.55

$$c_{11} = 3c_{12}; c_{13} = c_{44} \text{ not valid}$$

Crystal	c_{11} 10^{11} Dyn./cm ²	$3c_{12}$ 10^{11} Dyn./cm ²	c_{13} 10^{11} Dyn./cm ²	c_{44} 10^{11} Dyn./cm ²
Mg	5.65	6.96	1.81	1.68
Zn	16.3	7.65	5.08	3.79
Cd	12.1	14.4	4.42	1.85

that whilst polar (ionic) crystals show the relations which would be expected from their structures, the metallic crystals exhibit a gross lack of agreement. Since, however, there can hardly be any doubt as to the stability of these lattices, the only available explanation is that the second assumption, concerning the non-interaction of the component lattices, is not justified, and therefore the easily detachable electrons of the metals must be considered as independent constituents of the lattice.

2. TYPICAL CASES OF CRYSTAL PLASTICITY

Whilst as regards elastic behaviour, polar crystals agree with theory and only metallic crystals show a decided discrepancy, yet the plastic behaviour of both types differs most markedly from that indicated by theory.

(a) Slip

Slip is in the first place characterized by *the strictly crystallographic selection of the slip elements*, slip planes and direction. In general the preferred direction of slip is the line of greatest density in the lattice (in the case of polar crystals that most thickly beset with metallic ions), and the planes of slip are particularly densely packed planes of the lattice. Table 2 shows that the mechanical condition of maximum elastic shear can only play a subordinate part, if any, in the selection of the slip elements. As the examples in the table show, the actual slip systems (corresponding to those values printed in black type in the table) are not by any means always characterized by the maximum specific shear (elastic shear produced by unit shear stress).

Table 2. Slip systems and corresponding specific shears*: $\gamma = \tau/G$

(a) Cubic crystals:

Slip parallel to		Specific shear (1/G)	NaCl	KI	CaF ₂	Al	Cu	Au
Plane	Direction		(10 ⁻¹³ cm. ² /Dyn.)					
(001)	} [110]		s_{44}	78.0	238	29.6	35.2	13.3
(110)		$2(s_{11}-s_{12})$	56.0	89.2	16.8	43.4	42.6	66.1
(111)		$\frac{4}{3}(s_{11}-s_{12}) + \frac{1}{3}s_{44}$	63.3	138.7	21.1	40.6	32.8	51.7

(b) Hexagonal crystals:

Slip parallel to		Specific shear (1/G)	Mg	Zn	Cd
Plane	Direction		(10 ⁻¹³ cm. ² /Dyn.)		
(0001)	} [112̄0] [101̄0]	<i>s</i> ₄₄	59.5	26.4	54.0
(101̄0)		2 (<i>s</i> ₁₁ — <i>s</i> ₁₂)	60.0	14.6	27.6
(0001)		<i>s</i> ₄₄	59.5	26.4	54.0

* For notation and elastic constants see reference⁽³⁾.

Dynamically, slip is usually characterized by its very abrupt commencement in crystals at extraordinarily low stresses. After a small amount of purely elastic deformation and then of slight plastic deformation with accompanying rapid increase of stress, there follows a very large amount of deformation, sometimes accompanied even by a decrease in load. Figure 1 shows the well-defined nature of the "yield point" of crystals as thus defined, the example chosen being some creep-rate curves for cadmium crystals. The distinctness of the yield is often increased by the fact that at first it occurs locally and gradually extends over the whole crystal (see figure 2).

A quantitative law for the value of the yield point, which has been verified in all the cases hitherto investigated, asserts that the commencement of yielding is associated with the attainment of a definite *critical shear stress*⁽⁵⁾. A summary of the values of these critical stresses, determining the ease with which slip occurs in various materials, is given in table 3. The shear stress for slip systems other than the principal one is only known in the case of tin crystals. In this case there are four crystallographically distinct slip systems which have only slightly

different shear strengths; it thus follows that the possibility of slip is not entirely determined by the density of packing⁽⁶⁾. In general, however, the preference for the principal slip system is very marked, as may be seen from the variations in orientation over which it remains operative.

Figure 3 shows some data on the relation between critical shear stress and temperature in hexagonal metallic crystals. It will be seen that the shear strength

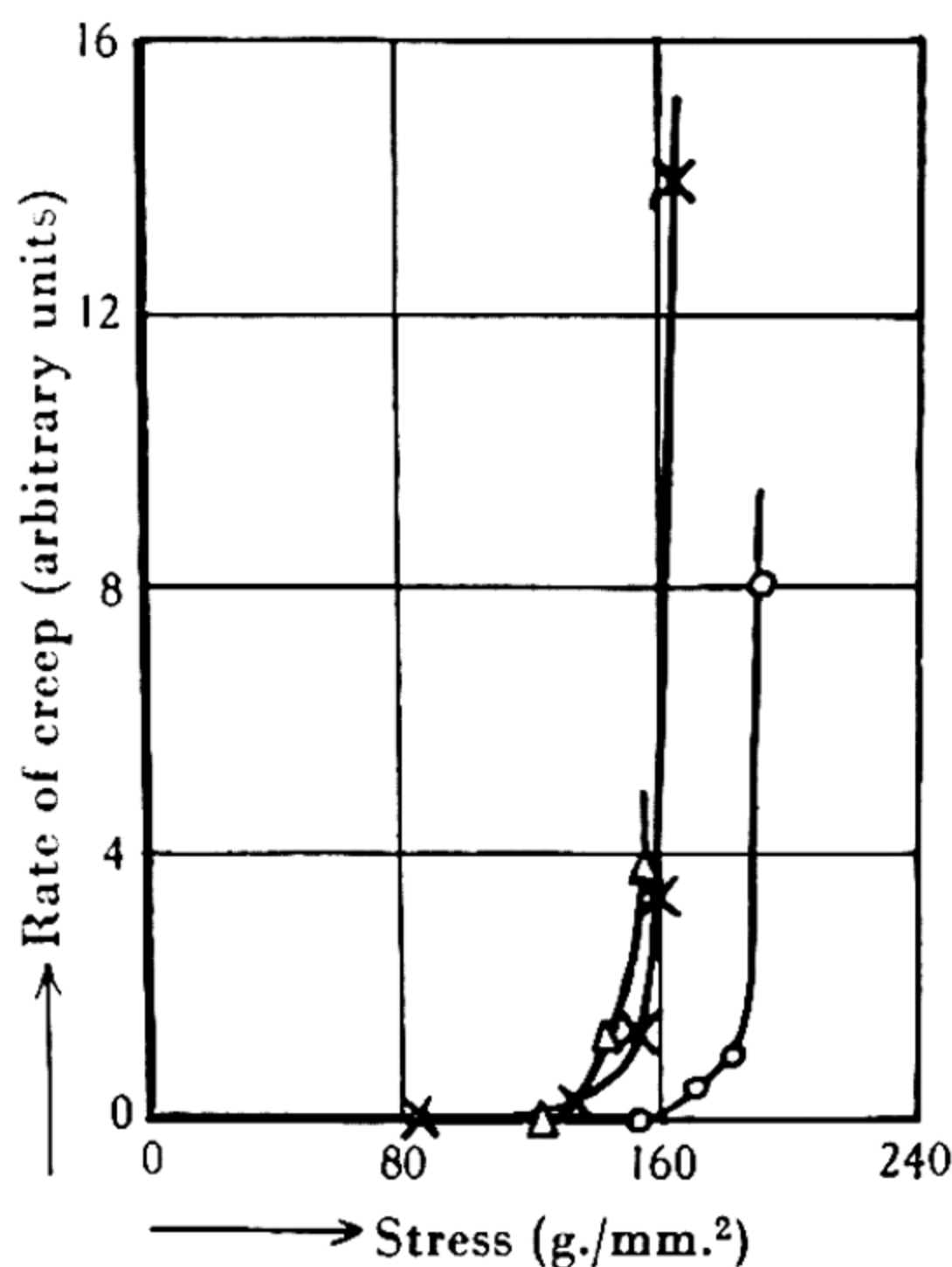


Figure 1. Distinctness of yield in Cd crystals.



Figure 2. Commencement of local extension in a Cd crystal (4).

of slip systems is only influenced to a small degree by the temperature. For example, the shear strength of the basal plane slip system of cadmium crystals is only increased about fourfold by decreasing the temperature from almost the melting point to 20° abs. Further cooling to 1° abs. has practically no effect⁽⁷⁾. Near the melting point, metals show a region of practically constant critical shear stress*. Similarly small effects of temperature on the commencement of plasticity have been observed in the case of the cubic metals aluminium⁽⁸⁾ and tungsten⁽⁹⁾. In order to investigate the plasticity of rock salt crystals at low temperatures, they have been subjected to torsion⁽⁹⁾. The results were very similar to those found in

* The effect of the variation with temperature of the solubility of impurities cannot yet be assessed separately.

metal crystals. The proportional limit in torsion, i.e. the stress at which deviation from Hooke's law first occurs, for the dodecahedral slip system, is found⁽⁹⁾ to be only 6 to 7 times as high at 20° abs. as at room temperature (see figure 4). Increasing

Table 3. Critical shear stresses of the principal slip systems of crystals (at 20° C.)

Crystal	Total impurities (parts per thousand)	Slip system		Critical stress g/mm ²
		Plane	Direction	
Cu	< 1	(111)	$[1\bar{1}0]$	100
Ag	0.1			60
Au	0.1			92
Ni	2.0			580
Mg	0.5	(0001)	$[11\bar{2}0]$	83
Zn	0.4			94
Cd	0.04			58
β -Sn	0.1	(100)	$[001]$	189
		(110)		133
Bi	~ 1	(111)	$[10\bar{1}]$	221
NaCl	0.3	(110)	$[1\bar{1}0]$	75
KCl	0.16			50
KBr	0.3			80
KI	0.2			70

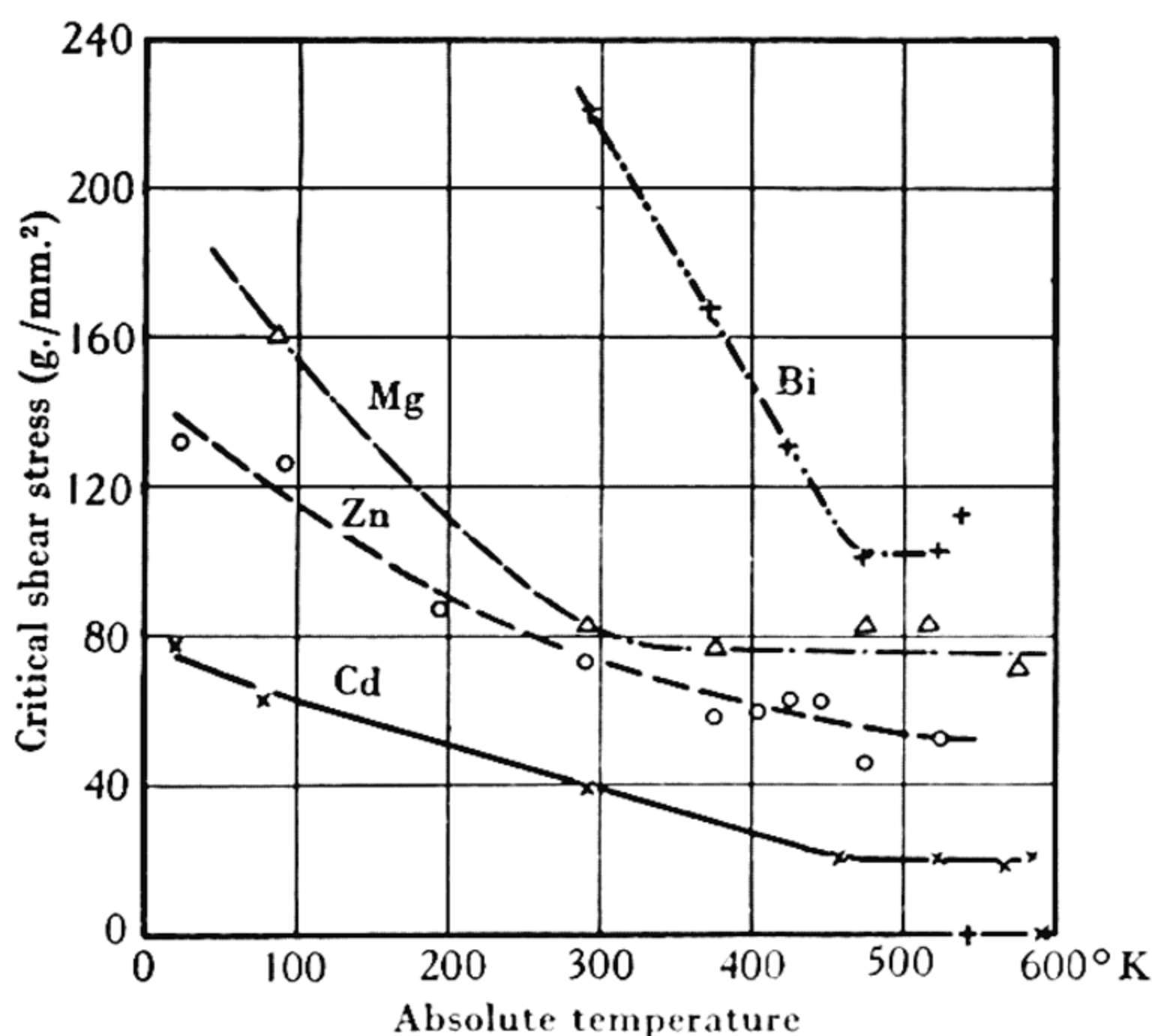


Figure 3. Relation between critical shear stress and temperature in metallic crystals⁽³⁾.

the temperature above 20° C. leads at first to an increase in shear strength, as had already been observed in tensile tests⁽¹⁰⁾. The fact that at higher temperatures new slip systems are sometimes observed (e.g. in Al, Mg, NaCl, BaSO₄) shows also that the alteration in shear strength is not uniform on all planes of the lattice.

Just as the yield point, which depends on the position of the slip elements, can be expressed by a single constant, the critical shear stress, so the course of the stress-strain curve, which depends on the orientation, can be expressed in a single

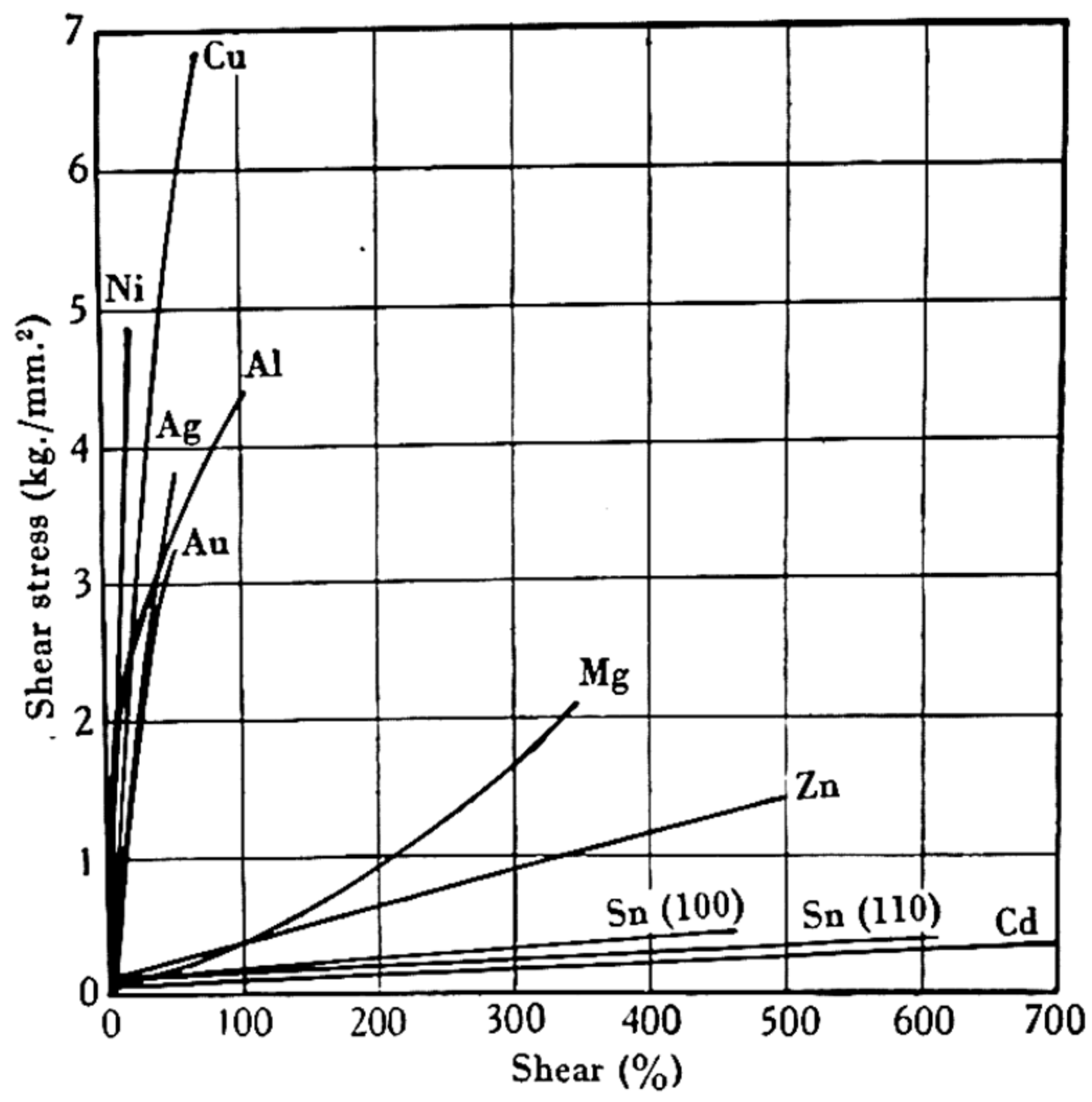
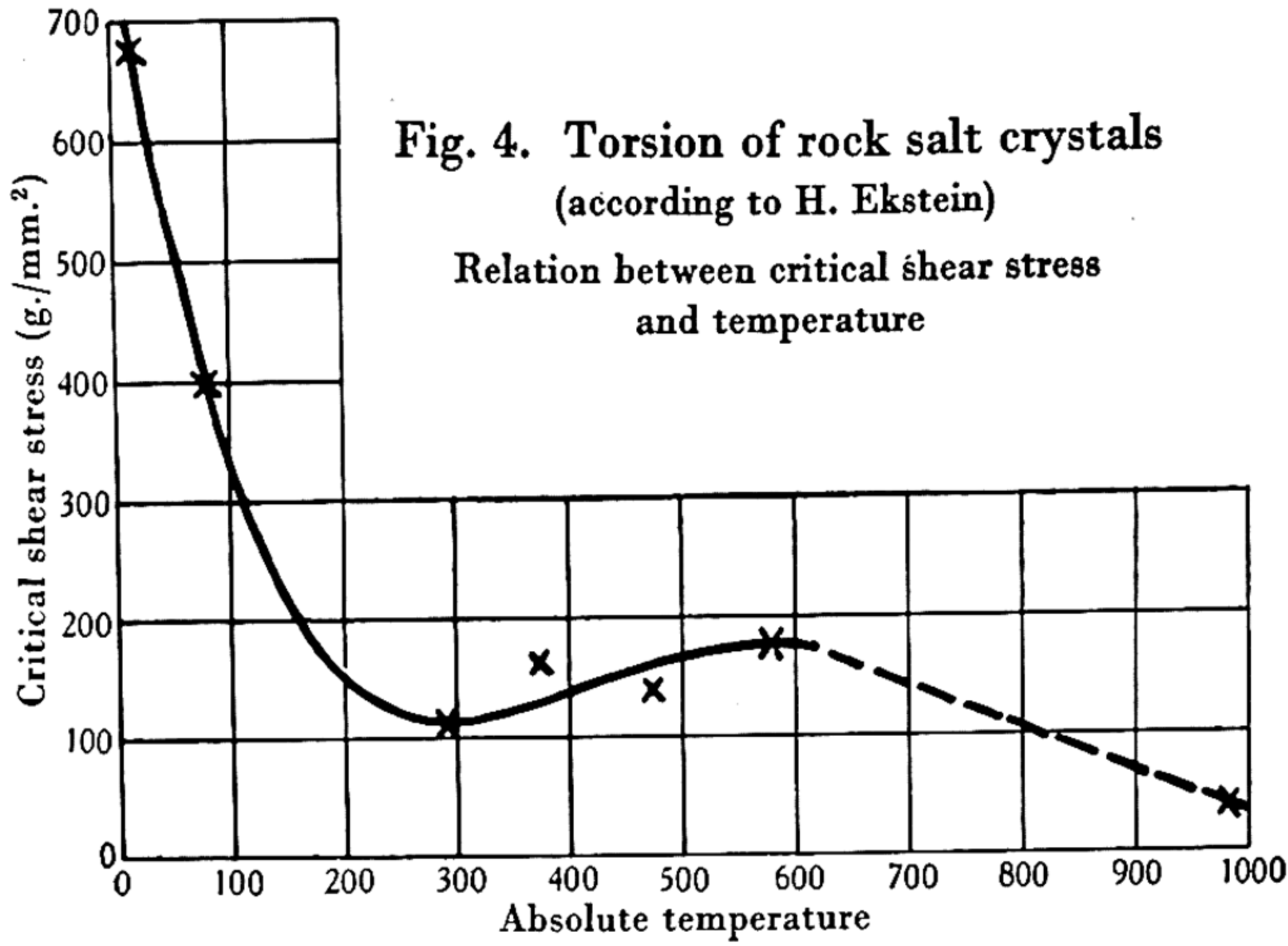


Figure 5. Hardening curves for metallic crystals.

curve, the “hardening curve” (*Verfestigungskurve*)⁽¹¹⁾. In this the shear strength of the operative slip-system is plotted as a function of the shear (relative displacement of two slip planes at unit distance apart); from it the hardening (increase in strength) of the crystal can be read directly. Figure 5 shows the form of the

hardening curve for crystals of all the pure metals so far investigated. The basal plane of hexagonal crystals (also the slip systems of tin) shows a much lower resistance to slip than the octahedral slip systems of the face-centred cubic metals. This cannot be regarded as due entirely to the difference in melting points, as the cases of aluminium and magnesium show. The very rough representation in figure 6 of the methods of two close packing of spheres may perhaps help to make plausible the very different behaviour of crystals of these two types (see also⁽¹²⁾). The upper half of the figure shows spheres piled in the two different ways; in the hexagonal close packing, the spheres in the third row (not shown in the figure) come vertically above those in the first row, whilst in the cubic close packing only the fourth row comes exactly over the first. In the lower half of the figure, sections are shown representing these planes for which the spheres, which for this purpose are taken

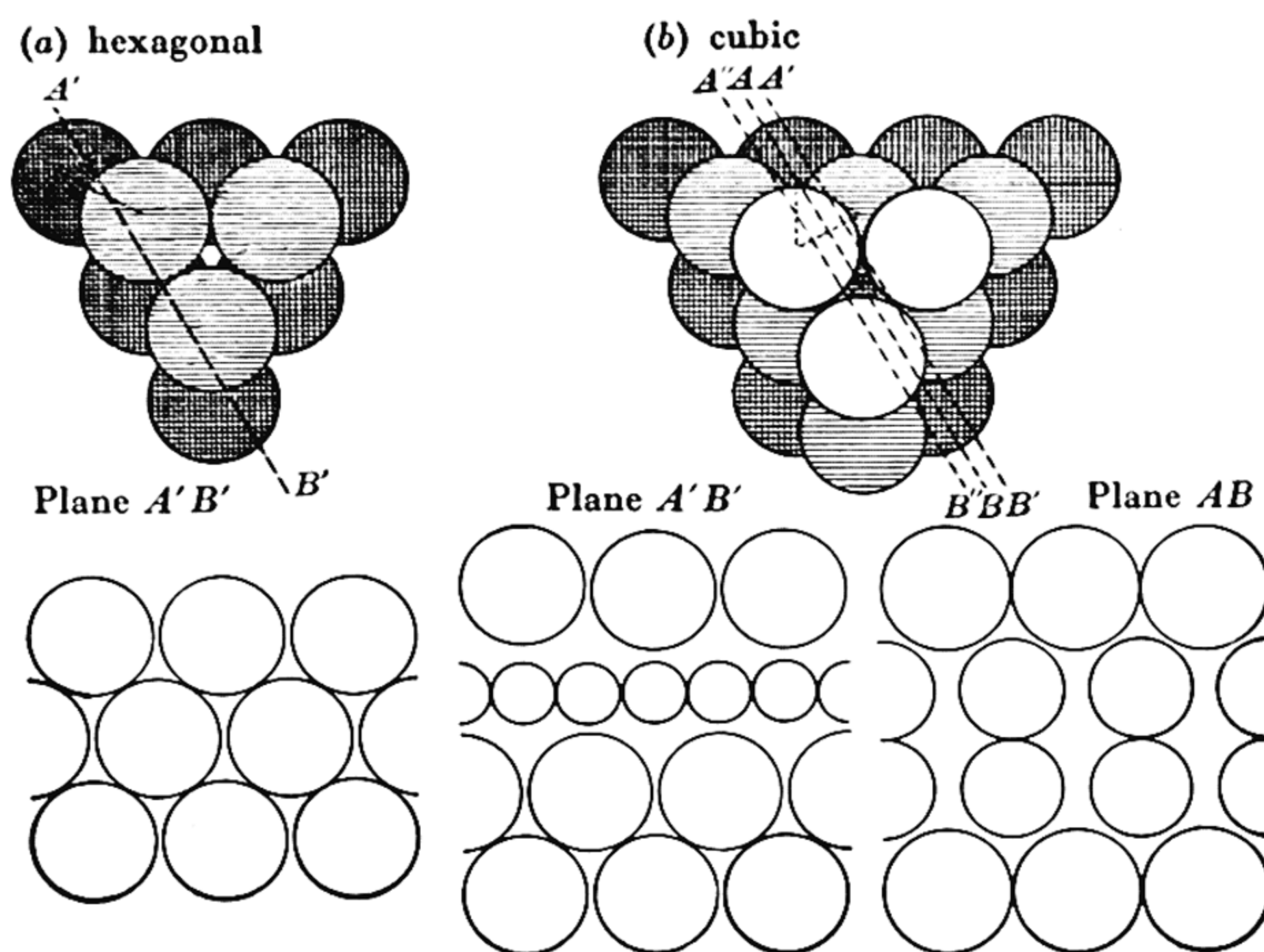


Figure 6. Slip in hexagonal and cubic close packed crystals.

to represent atoms, undergo slip*. The behaviour of hexagonal crystals is seen to be much simpler than that of cubic crystals.

In polar crystals also, deformation is accompanied by considerable strengthening of the crystal. Quantitative hardening curves have however not yet been obtained. This is due to the fact that, in the crystals of the rock-salt type to which most attention has so far been devoted, the crystallographic identity of the slip direction with the normal to the slip plane causes duplex slip to occur even at the commencement of the normal tensile test⁽¹³⁾. Crystals of the caesium chloride type (slip plane (110), direction [001]) should form suitable material for such an investigation.

The effect of temperature on the hardening curve is very slight at high or low temperatures, but very considerable in the middle range. Here there is a transition from the steep curve at low temperatures, indicating considerable hardening, to the flat curve obtained at high temperatures⁽¹⁴⁾.

* The section $A''B''$ is obtained from $A'B'$ by exchange of the two middle rows.

What conditions govern the *cessation of slip* cannot yet be stated with certainty. The type of phenomenon following slip (mechanical twinning, cleavage, or the development of a tic or of a crack) certainly plays an important part. With regard to the very illuminating condition put forward as a result of alternating bending tests on steels⁽¹⁵⁾ and static torsion and compression tests on copper⁽¹⁶⁾, namely, that failure occurs when the material has absorbed a certain amount of internal energy, it may be said that corresponding test results on single crystals are not available. Tests on zinc crystals, which have shown⁽¹⁷⁾ that prior deformation in alternating torsion increases very considerably the energy absorbed to fracture in tension, do not necessarily disprove this energy hypothesis, as the heat evolved was not measured.

(b) *Mechanical twinning*

Our knowledge of the second typical crystallographic deformation phenomenon, the mechanical development of twins, is still practically limited to the crystallographic nature of the twinning elements. This type of deformation, which consists in portions of the crystal taking up positions symmetrical to the original lattice about the twinning element, extends in general in a way which is macroscopically discontinuous. Frequently the transition to the twinned state occurs so rapidly that the deformation is accompanied by loud reports. The stresses necessary to cause twinning are of the same low order as those necessary for slip. No quantitative dynamical condition for the initiation of twinning is yet known. This is due in the first place to the very marked sensitivity of twin formation to the presence of inhomogeneity; for this reason mechanical twinning always occurs over a more or less wide variation in stress. In the second place, twinning is often accompanied and disturbed by slip.

The effect of temperature on twinning appears to be still smaller than that on slip, as is shown by the failure of twinning at high temperatures in zinc and cadmium, and by the occurrence of twinning in preference to slip at low temperatures in α -iron.

Twinning, like slip, leads to strengthening of the crystal. For instance, the shear strengths on the basal plane of twin lamellae of zinc and cadmium crystals at room temperature are increased about twofold⁽¹⁸⁾ and threefold⁽⁴⁾ respectively. In agreement with this, twin lamellae form extremely favourable centres for recrystallization (see figure 7). For example, annealing at temperatures over 145° C. for 1 min. always produces recrystallization in twin lamellae of strained cadmium crystals, whilst in the twin-free areas a temperature of at least 240° C. is necessary.

In considering the theoretical aspects of these two mechanisms of deformation, it may be remarked that it is now well established that *the observed low strengths on the slip and twinning planes cannot be regarded as the strength of the lattice**. Variations in the modulus of rigidity have never been observed at stresses below the onset of plastic deformation; the elastic shear at the yield point or at the commencement of twinning is of the order of 10^{-4} and not about 0.5 of that necessary for the overcoming of the shear strength of the lattice. Opinions are

* The same may be said of the tensile strength of crystals (not dealt with here).

still widely divergent as to the reasons for this premature failure in crystals and for the strengthening which accompanies deformation. *Lack of structural and of thermal homogeneity* have been regarded as responsible, both separately and in combination. In general, recent opinion in the case of slip (see particularly^(19, 20, 21)) is that the slip does not occur simultaneously throughout the whole cross-section of the crystal, but only locally in small regions, afterwards spreading through the whole

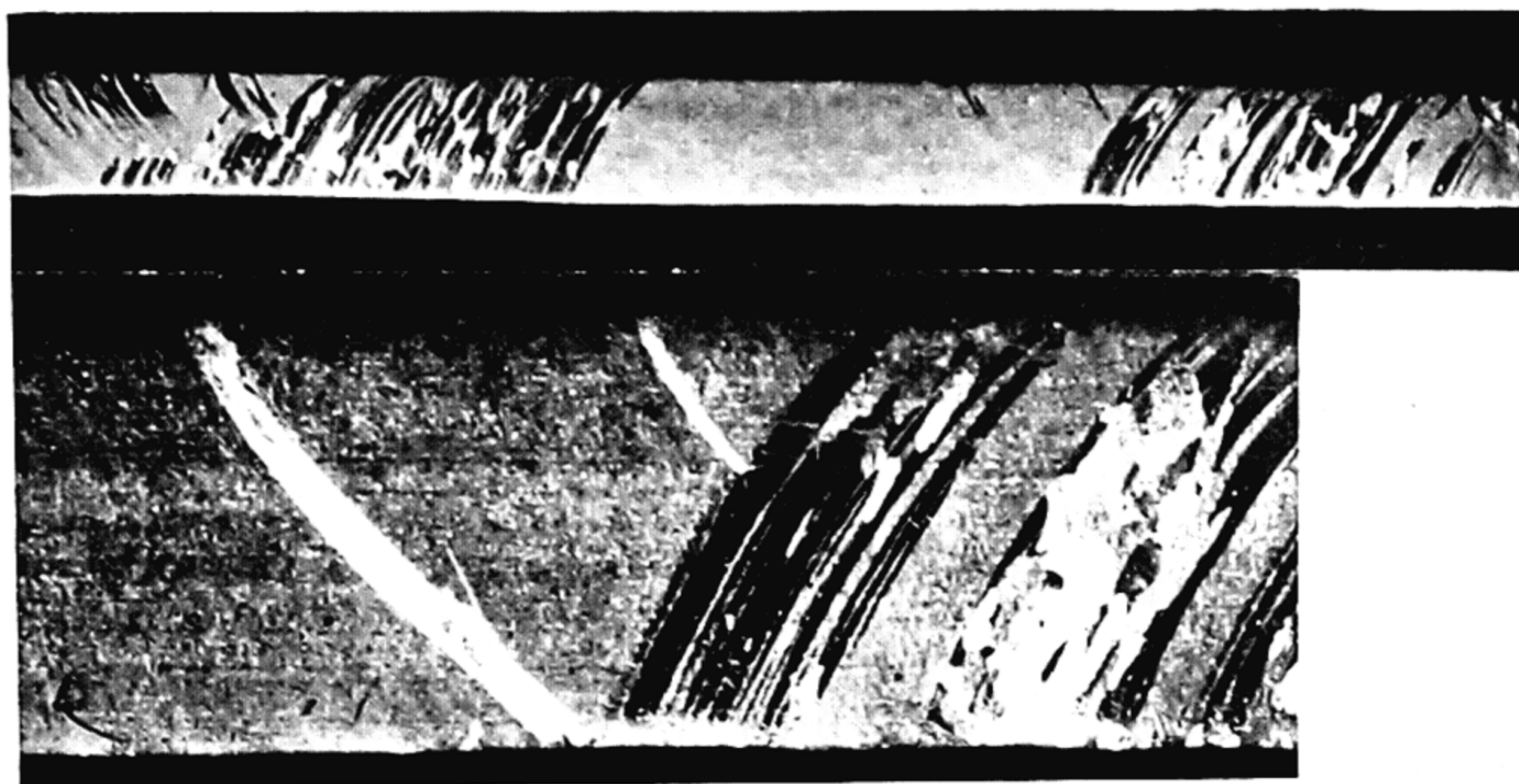


Figure 7. Recrystallization of strained Cd crystal commencing from twin lamellae.

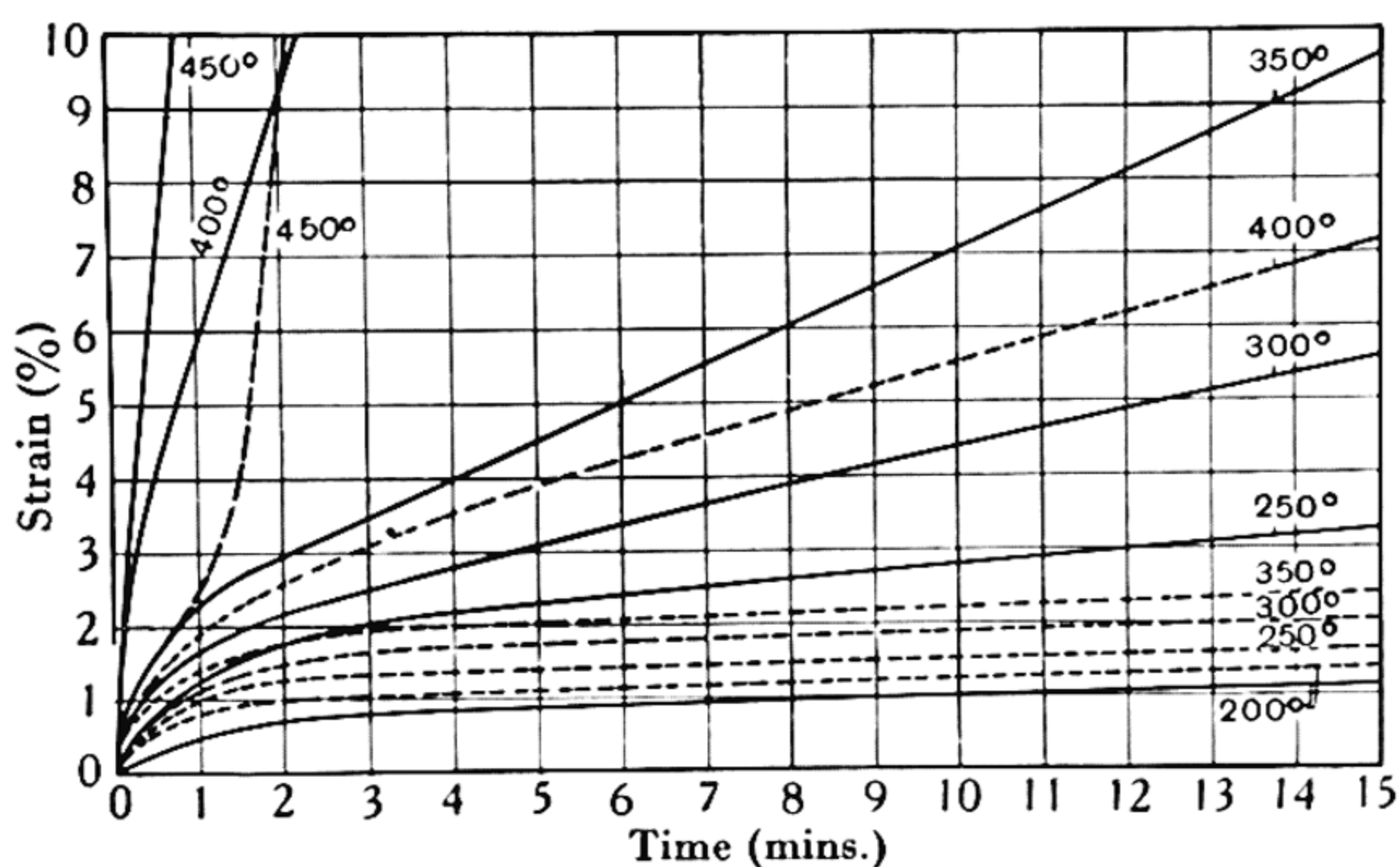


Figure 8. Effect of temperature on creep curves of hard and soft copper wire⁽²⁴⁾.
Stress 1.6 kg./mm²

— hard - - - soft.

crystal. That similar diffusion phenomena, depending on the slip system and the induced stresses, may also be taken as a model of twin formation is, however, hardly likely. In this case, the attainment of stable equilibrium necessitates that all the atoms in the neighbourhood of a particular atom shall change their positions simultaneously.

3. NON-CRYSTALLOGRAPHIC PLASTICITY

A special type of plasticity, which probably cannot be regarded as due to crystallographic slip motion, is shown by crystalline materials when sudden changes

of position occur (e.g. in recrystallization or phase change). Under the influence of external stresses that type of position-change will naturally be preferred (as in the case of plasticity in amorphous bodies) which results in a reduction of stress or plastic deformation, according to the applied load. In this way a recrystallized and therefore soft, annealed material may, above the recrystallization temperature, be stronger and more resistant than the hardened material, in which sudden changes of position take place on heating⁽²²⁾. Tests on spirals of tungsten⁽²³⁾ and on wires of aluminium and copper⁽²⁴⁾ do in fact show considerable creep when recrystallization occurs. As an example, figure 8 shows creep curves at high temperatures for hard and soft (annealed at 600° C.) copper wires; in all cases the hard, recrystallizing wire creeps more than the soft annealed wire. Similar results have also been found in the investigation of the "creep strength" of iron, nickel and various alloys of these metals at elevated temperatures⁽²⁵⁾. The significance of this fact in practice is self-evident.

Detailed investigation of the phase change has been carried out in an iron-nickel alloy (30 per cent Ni)⁽²⁶⁾. If by cooling, the change from the (face-centred cubic) γ -phase to the (body-centred) α -phase occurred while the wire was under stress, it was accompanied by extensions up to 10 per cent. In this case also the change of position of the atoms is associated with a mechanically weak state.

REFERENCES

- (1) M. BORN. *Probleme der Atomdynamik*, p. 136 (Berlin, 1926).
- (2) P. P. EWALD. In Müller-Pouillet, *Lehrb. d. Physik*, 1/2, 11th ed. p. 936.
- (3) E. SCHMID and W. BOAS. *Kristallplastizität* (Berlin, 1935); see the bibliography given in this book.
- (4) W. BOAS and E. SCHMID. *Z. f. Phys.* **54**, 16 (1929).
- (5) E. SCHMID. *Proc. Int. Congr. Appl. Mech.* Delft 1924, p. 342.
- (6) I. OBINATA and E. SCHMID. *Z. f. Phys.* **82**, 224 (1933).
- (7) W. MEISSNER, M. POLANYI and E. SCHMID. *Z. f. Phys.* **66**, 477 (1930).
- (8) W. BOAS and E. SCHMID. *Z. f. Phys.* **71**, 703 (1931).
- (9) H. EKSTEIN. Unpublished.
- (10) W. THEILE. *Z. f. Phys.* **75**, 763 (1932).
- (11) R. KARNOP and G. SACHS. *Z. f. Phys.* **41**, 116 (1927); E. SCHMID, *ibid.* **40**, 54 (1926).
- (12) H. G. SOSSINKA, B. SCHMIDT and F. SAUERWALD. *Z. f. Phys.* **85**, 761 (1933).
- (13) E. SCHMID and O. VAUPEL. *Z. f. Phys.* **56**, 308 (1929).
- (14) M. POLANYI and E. SCHMID. *Naturw.* **17**, 301 (1929); W. BOAS and E. SCHMID, *Z. f. Phys.* **61**, 767 (1930); see also (7).
- (15) A. ONO. *Proc. 3rd Int. Congr. Appl. Mech. Stockholm*, **2**, 305 (1930).
- (16) G. I. TAYLOR and H. QUINNEY. *Proc. R.S.* **143**, 9 (1934).
- (17) E. SCHMID. *Z. f. Metkde*, **20**, 69 (1928).
- (18) E. SCHMID and G. WASSERMANN. *Z. f. Phys.* **48**, 370 (1928).
- (19) G. I. TAYLOR. *Proc. R.S.* **145**, 362, 388, 405 (1934).
- (20) E. OROWAN. *Z. f. Phys.* **89**, 605, 614, 634 (1934).
- (21) M. POLANYI. *Z. f. Phys.* **89**, 660 (1934).
- (22) R. BECKER. *Z. f. techn. Phys.* **7**, 547 (1926).
- (23) F. KOREF. *Z. f. techn. Phys.* **7**, 544 (1926).
- (24) E. SCHMID and G. WASSERMANN. *Z. f. Metkde*, **23**, 242 (1931).
- (25) W. ROHN. *Z. f. Metkde*, **24**, 127 (1932).
- (26) G. WASSERMANN. *Arch f. Eisenhüttenwesen*, **8**, 347 (1932-33).

DISCUSSION

Dr H. J. GOUGH. The papers to which we have listened deal with the discrepancy that apparently exists between the theoretical strengths of solids and their observed strengths as determined under *static* tests to destruction. Yet if we choose suitable *cyclic* stress conditions, solids—and particularly metals—can be fractured under repetitions of a stress which is only about 50 per cent of the usual value of the practical strength. This type of failure—which for want of a better term is called “fatigue” failure—possesses features which render it of special interest in the present connexion, quite apart from its importance in engineering construction. A striking characteristic is that even the most ductile metals fracture in an apparently brittle manner; no appreciable change of general shape occurs, but fracture results from a spreading crack. Detailed study of fatigue cracking has established that this failure originates in local regions: it is found that, in a piece of metal consisting of hundreds of millions of crystals, cracking commences in a very few isolated crystals and spreads from these centres: it has also been established that these centres represent crystals which have suffered considerable plastic deformation by slip. The extension of this study of fatigue to single crystals of ductile metals, such as aluminium, copper, silver, zinc, iron, etc., has revealed that the process of failure is exactly similar to that of crystalline aggregates, while the use of microscopical and X-ray methods has enabled the characteristics of failure to be correlated with the crystalline structure. In every case investigated, cracking has originated on the site of slip bands which represented slipping, under cyclic shearing forces, on definite crystallographic planes and in definite crystallographic directions. But of the available slip planes, slip actually occurs on a few only, while the slip bands do not extend right across the crystal but are of short length: the pitch, or distance apart, of the slip bands decreases with increasing range of applied shear stress. Now, although fatigue cracks always originate on the site of slip bands, yet cracking is not inseparably associated with slip, for, provided the applied range of stress has less than a certain limiting value, slip ceases, hardening is effected and fracture does *not* result. When this limiting value is exceeded, however, cracking can be observed to commence, leading to complete fracture. *Cracking is, therefore, a local effect and is a consequence of previous plastic deformation.* The changes in the nature of the X-ray reflexions obtained from crystals plastically deformed under cyclic stresses suggest that the crystal structure thereby becomes distorted or broken up in a manner which is equivalent to rotations of parts of the crystal about an axis contained by the slip plane and perpendicular to the slip direction, and it is reasonable to suppose that in this manner stresses are set up of an altogether different order of intensity from the average stress estimated merely from the externally applied load and the total dimensions of the specimen. *Thus, the actual stresses causing rupture may conceivably approximate to what are sometimes assumed to be the theoretical strengths of metals.* Experiments are now in hand to determine if a quantitative estimate can be obtained by the aid of X-ray methods of precision for the intensity of the strains induced in these local regions.

It will be seen that the above tentative conclusions derived from the study of the fatigue characteristics of metals bear many general points of resemblance to those reached by other researchers dealing with the rupture strength of solids under static forces. It is interesting to note that entirely different and independent methods of attack upon what appear to be two distinct problems converge in a very satisfactory manner upon the basic problem of cohesion.

The question now arises: Must the initial low resistance of metals to plastic deformation be ascribed to an imperfect structure, requiring the assumption of intrinsic flaws, loose structures or mosaic structures? If the strengths of metals are to be calculated from the forces necessary to separate atom entirely from atom, then such assumptions may, perhaps, become necessary and permissible. But metals deform by shear and, as far as I am aware, no estimate has yet been made of their resistance to sliding. At the present time, it appears to me that existing knowledge of the cohesive forces of the "metallic" types of combination is much too incomplete to warrant definite statements concerning the theoretical strengths of metals. A closely associated and highly important aspect of the strength of metals, of which too little is known, is that of the process of strain hardening: crystal break-up, lattice distortion, and preferred orientation all fail to offer an adequate explanation. Changes in the distribution of the free electrons have been suggested as the primary cause of the hardening of metals, and if this proves to be the case, fundamental knowledge of the true nature of slip may become available. In any case, the non-satisfaction of the Cauchy relations seems to indicate quite clearly that the inter-atomic forces are not purely central forces depending only on the atoms themselves.

Thus, until quite recently, a fair statement of the position would have been that the observed characteristics of the deformation of metals appeared to be *consistent* with the theories of Intrinsic Flaws *or* of Loose Structure *or* of Mosaic Structure, but that none of these was sufficiently definite to enable us to construct a *quantitative* theory to account for the finer and more important characteristics of the deformation and fracture of ductile metals. In my opinion, however, the recent theory of Prof. Taylor has profoundly altered our outlook on the whole problem. By assuming the presence of random dislocations, probably due to thermal oscillations, and applying the methods of the theory of elasticity, he has constructed a quantitative theory which leads to conclusions regarding slip, strain hardening, the local strains resulting from slip, the elastic limit, and the influence of the test temperature upon these and other characteristics of plastic deformation, which are in marked general agreement with the results of observation. The fact that *some* crystals give shear stress-strain relations which do not conform to the parabolic form predicted by the theory is not, I suggest, of great importance at the present stage of development of the theory. One of the most interesting aspects of Prof. Taylor's theory is that it requires, as an essential, the presence within the crystal of some type of "interference structure" to limit the path of the migrating dislocations: he has shown that the dimensions of this structure are of the same order as that of the "secondary" structure of whose existence so much circumstantial evidence of a variety of types has been obtained.

Lest I be misunderstood, I firmly believe that we should preserve entirely open minds on all theories, however attractive, which assume that the existence of imperfect structures is required to explain the characteristics of solids, *until after the nature of their cohesive forces has been clearly determined and shown to demand the existence of such imperfections*. At the present time, however, no such fundamental foundation exists, and until this has been provided by the mathematical physicists, it is extremely helpful to build up tentative theories with which to compare the results of observation and experiment. In this direction Prof. Taylor has made a notable contribution to our knowledge of the subject, and I venture to express the hope that he will continue to explore the implications of his theory.

Prof. E. N. da C. ANDRADE. During the last few years a number of investigations have been carried out in my laboratory on single crystals of metals, with special reference to the purity of the metal, in particular with cadmium and mercury. The work on cadmium was begun in conjunction with Dr Chalmers, and continued in conjunction with Dr Roscoe, while Mr Hutchings and Mr Greenland have co-operated in the work on mercury. Mercury was chosen since not only can it be prepared free from metallic contamination to a very high degree⁽¹⁾ (impurities not exceeding 1 part in 10^8), but it is also free from dust and dissolved gases, both of which have been mentioned as causes likely to lead to departures from the perfect lattice. Perhaps I may be allowed to mention that I prepared single crystals of mercury, and of other metals, early in 1914⁽²⁾.

Single crystals of cadmium, lead and bismuth have been prepared by the use of a narrow furnace which travels along relative to the wire: with a suitable relation between the temperature gradient and the velocity of travel, single crystal wires can be produced which give much more constant results than, e.g., those prepared by the Czochralski method, used by Boas and Schmid⁽³⁾. With crystals of cadmium prepared by this method the law of critical shear stress, referred to by Dr Schmid, has been confirmed to a closer degree than hitherto. The resolved shear stress does not depend upon the rate at which the crystal is grown, so long as it is a single crystal: with the Czochralski crystals this is not the case.

Dr Roscoe⁽⁴⁾ has made a remarkable observation on the effect of surface in cadmium crystals. With a superficial layer of oxide one or two molecules thick, the critical shear stress may be as high as twice the value obtained with a clean surface. If the oxide is dissolved off half a single crystal wire, we may have considerably different critical shear stresses in two parts of the same wire; other experiments show that it does not matter whether the oxide film is formed during the growth of the crystal, or subsequently. Frequent reference has been made to-day to the effect of treatment of the surface on the strength of rock salt crystals, but this appears to be the first time that a surface influence has been recorded with metals. No doubt with a clean surface the initial slip which takes place at the critical shear stress is due to minute cracks in the surface, much as has been described by Dr Orowan for rock salt, and the effect of the oxide layer is to round off and strengthen the sharp edges at which the stress is high.

The cadmium used by us contained initially some 0.11 per cent zinc and 0.03 per cent lead as impurities. Further purification reduced both the critical shear stress and the plastic hardening, measured by the slope of curve of resolved shear stress against shear (see E. Schmid, figure 5). With our purest cadmium at room temperature the critical shear stress was 13.7 g./mm². With our purest mercury at -50° C. it was 9.3 g./mm², while for very pure zinc Hanson⁽⁵⁾ has recently found 9.1 g./mm². All the values are of a lower order than those given by Dr Schmid, being not much more than a tenth of his. There is an indication that the value may be about the same for all metals. We propose to investigate the change of critical shear stress with temperature for very pure metals, and also to carry out experiments with a metal deliberately contaminated with small amounts of a foreign metal, in order to extrapolate to absolute purity. It is important to know if the critical stress tends to a finite value.

With cadmium, Dr Roscoe and I have found that the two impurities present, zinc and lead, have each a different effect. Small quantities of lead increase the critical shear stress, while small quantities of zinc increase the plastic hardening. While lead crystallizes in cubic form, zinc, like the cadmium, is hexagonal. It is possible that the thermal diffusion of lead atoms takes place less readily than that of zinc atoms, which, from the work of W. L. Bragg and E. J. Williams⁽⁶⁾ on the behaviour of alloys in which both metals belong to the same type of lattice, would be expected to move about freely to the positions of minimum potential energy. The sharp corners of internal flaws appear from the type of consideration put forward by Kossel and Stranski to be such positions. Lead atoms may be able to diffuse to the surface because of the greater freedom of thermal movement near the surface, in a tangential direction, of planes intersecting the surface.

Mercury⁽¹³⁾ at about -50° C. shows well-marked glide, the glide planes being particularly sharp, as can be seen from figures 1 and 2, which represent respectively an early and a later stage of glide in the same crystal. An addition of 0.5 per cent of silver raises the critical shear stress considerably, but does not affect the spacing of the glide planes. These, however, lose their sharpness, and appear diffuse, as seen in figure 3. This suggests that the impurities tend to diffuse to the glide planes. There are many points of interest about mercury. It crystallizes on the rhombohedral system, and doubt has been expressed⁽⁷⁾ as to whether glide, as distinct from twinning, can be obtained from crystals of this system. We have found that mercury glides on the rhombohedral faces, the glide direction being the short diagonal, and no sign of glide on the hexagonal base has ever been obtained by us, although this has been suspected of being the glide plane for tellurium⁽⁸⁾, which is also rhombohedral. With mercury the rhombohedral face and the hexagonal base are planes packed equally closely, within the experimental error of the angle determination, but the rhombohedral face contains a much more closely packed line, which is possibly the deciding factor. No other case seems to be known where these conditions prevail. Mercury twins on the plane through the long diagonals of the opposite faces, figure 4 being given as an example of the appearance of a twinning boundary. In all cases where the projection of the glide direction coincided approximately

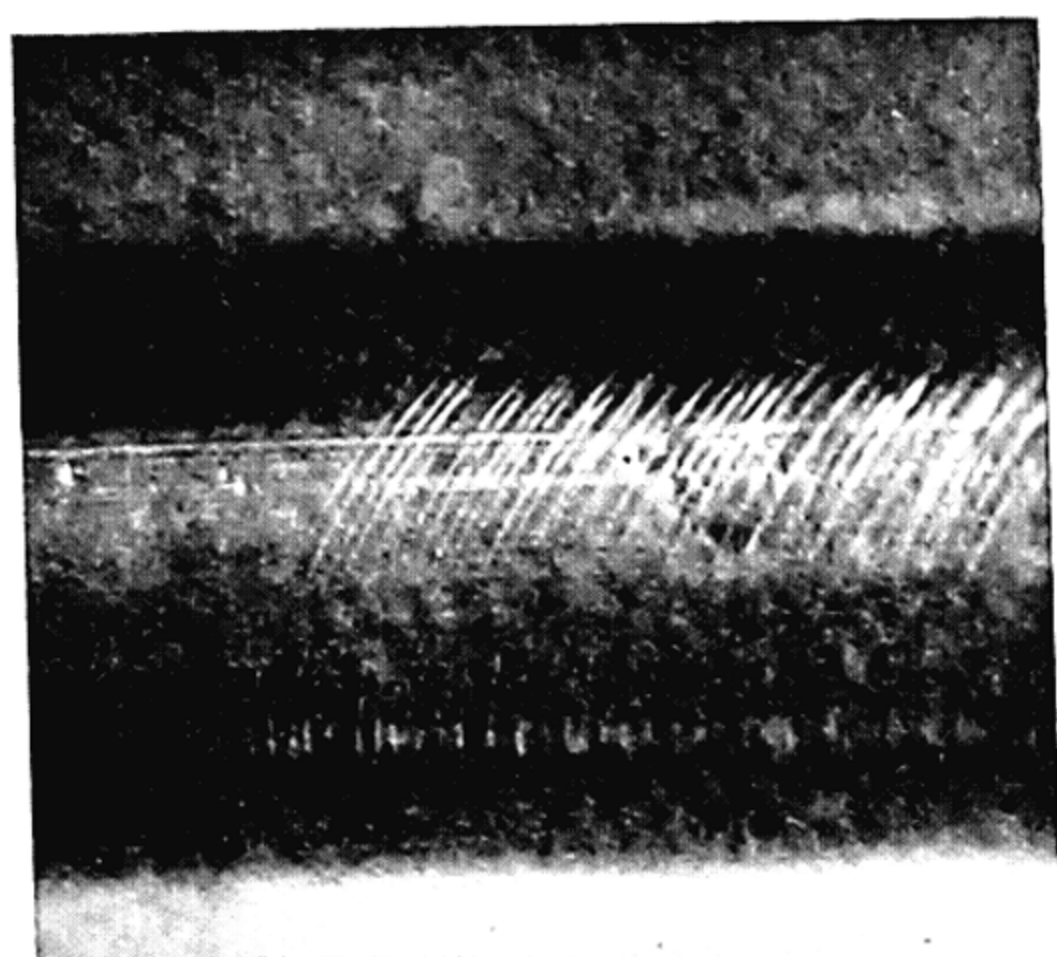


Figure 1. Glide planes on pure mercury:
early stage.

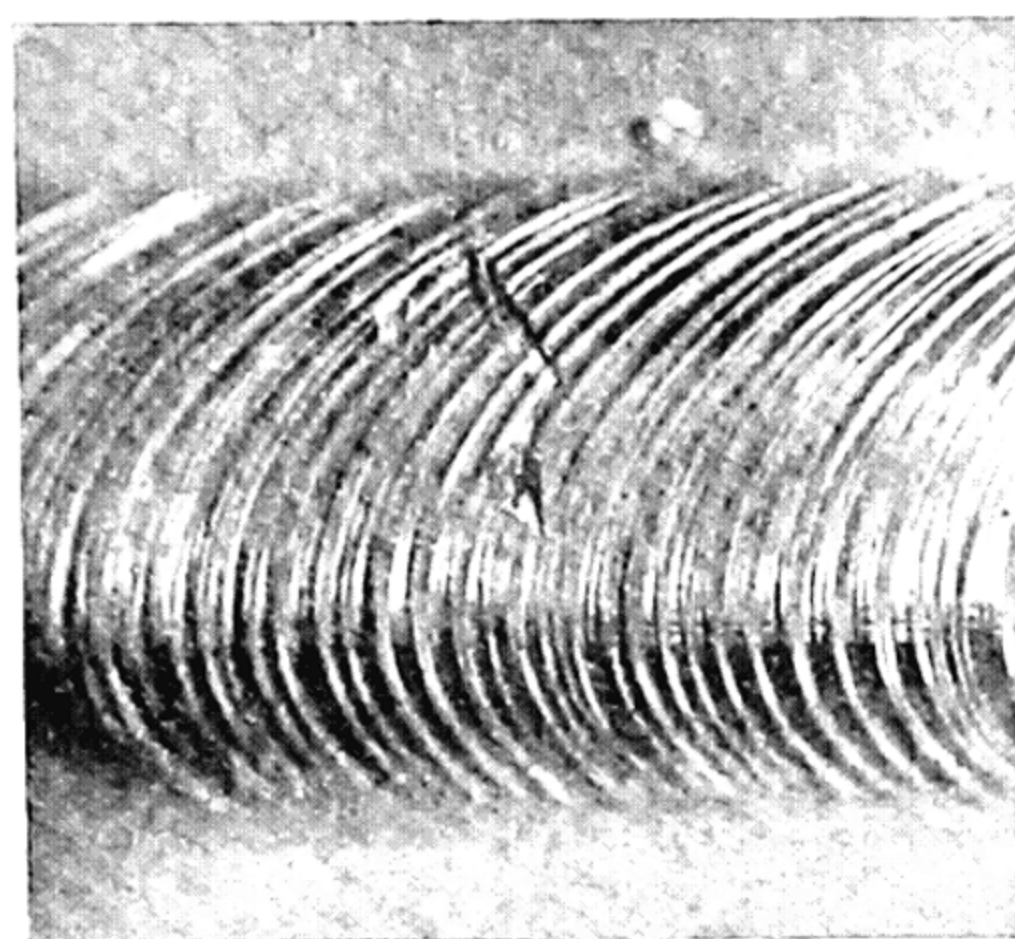


Figure 2. Glide planes on pure mercury:
late stage.

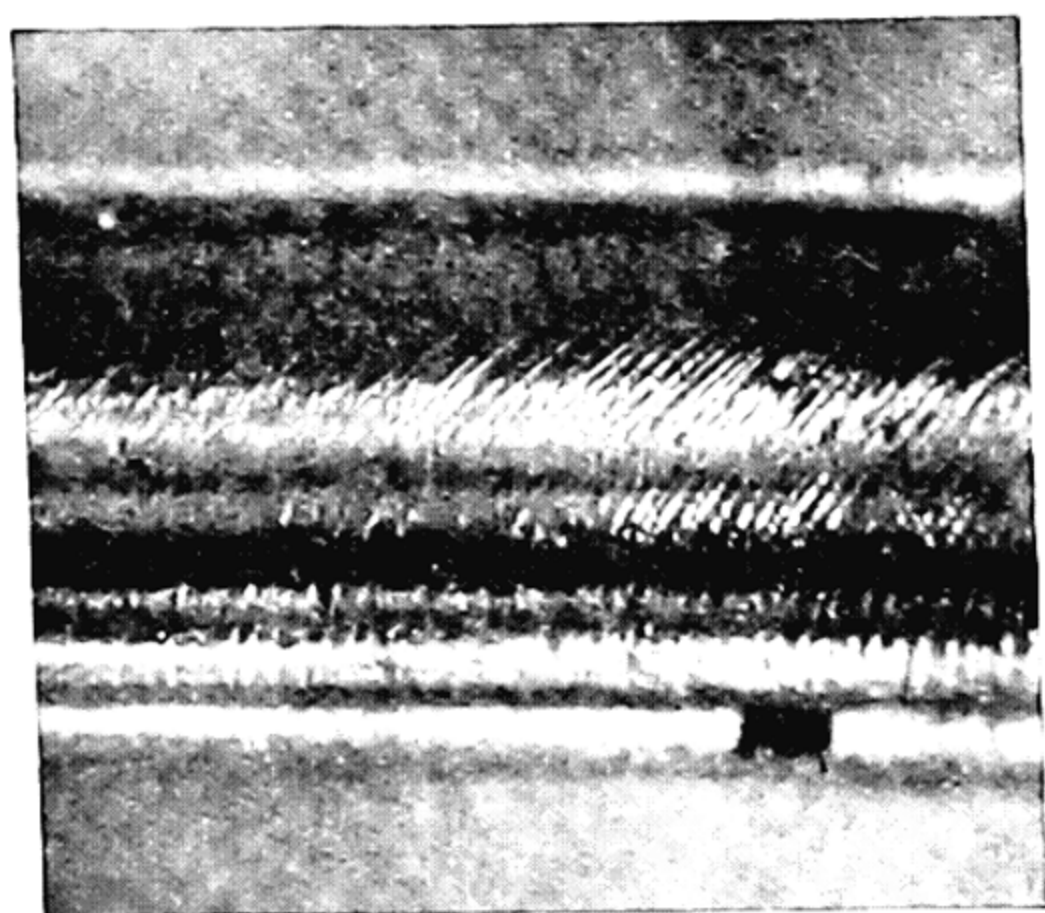


Figure 3. Glide planes on mercury
containing 0.5 % silver.

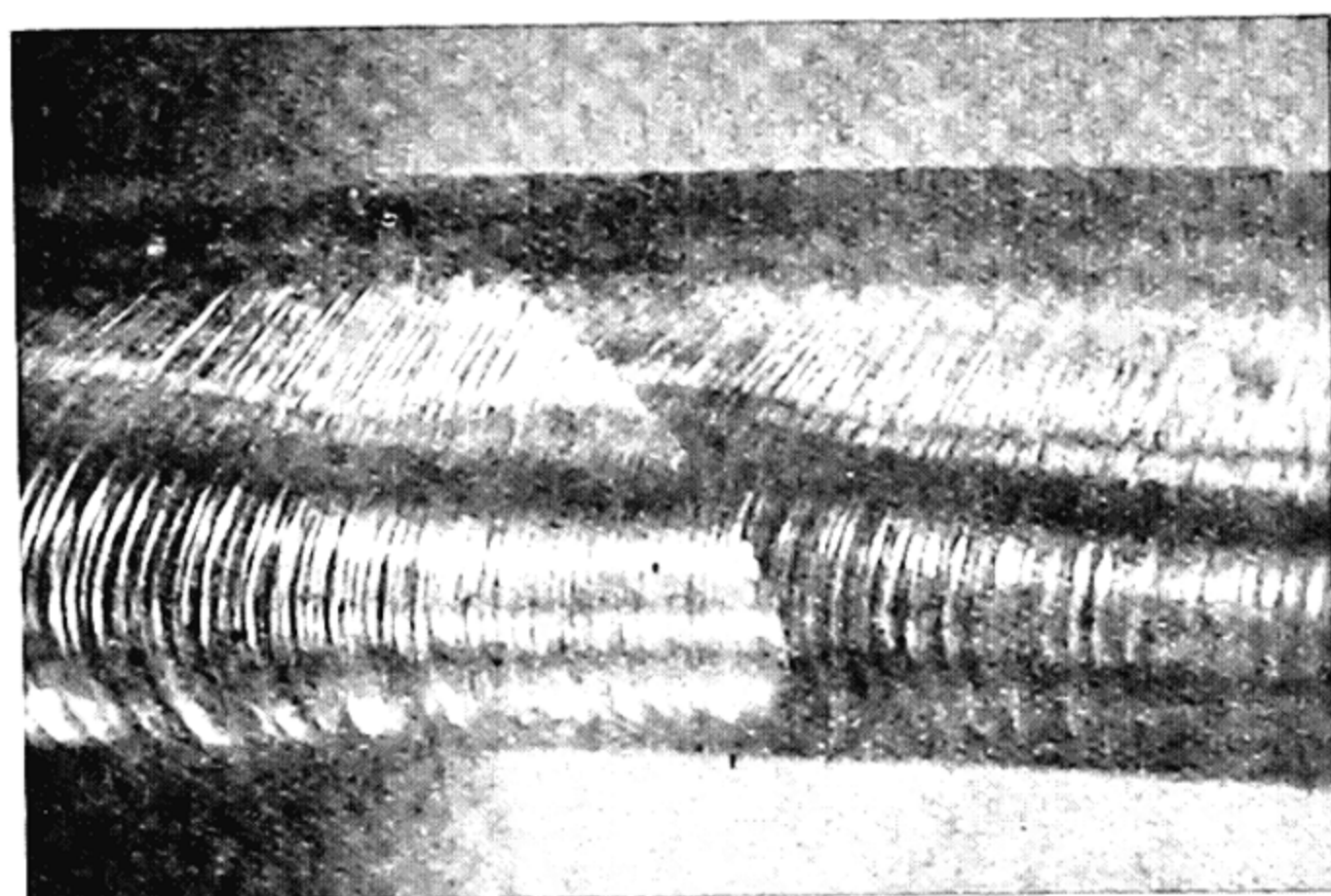


Figure 4. Twinning boundary on mercury at
 -50°C .

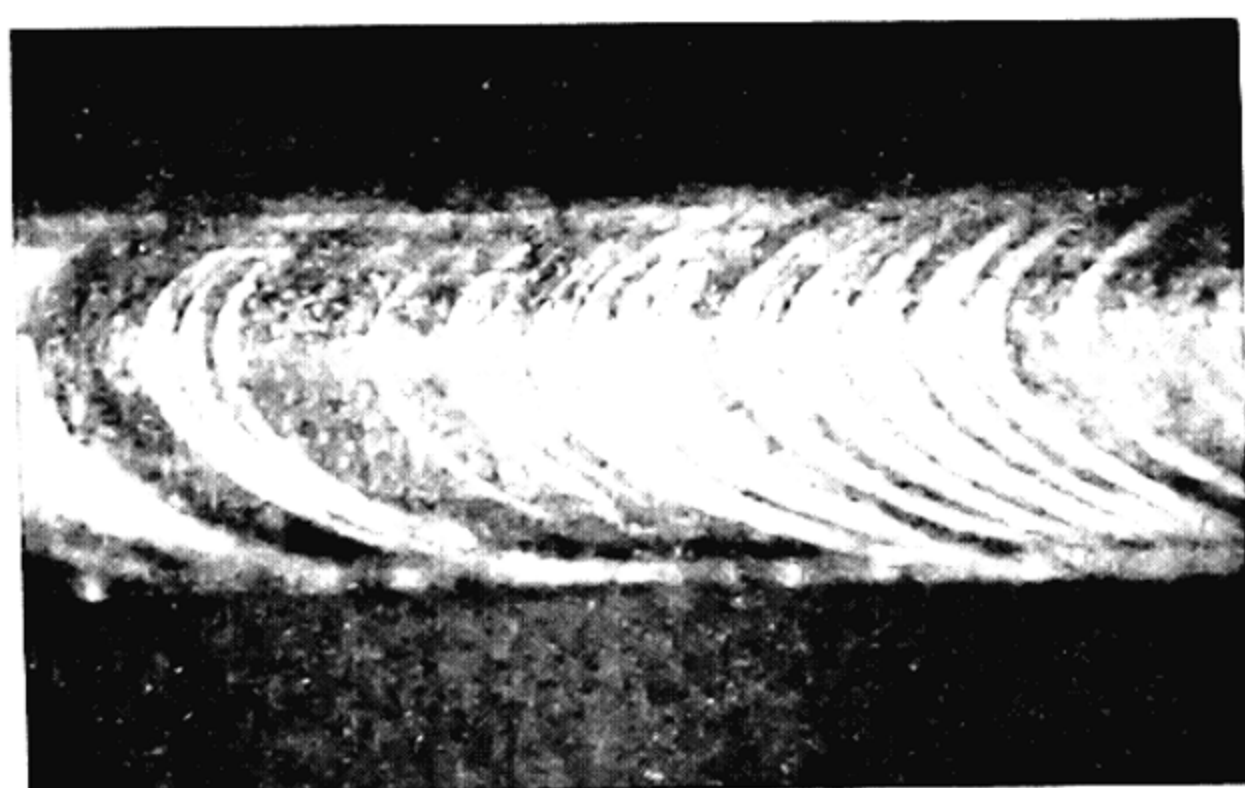


Figure 5. Twinning bands on mercury
at -180°C .

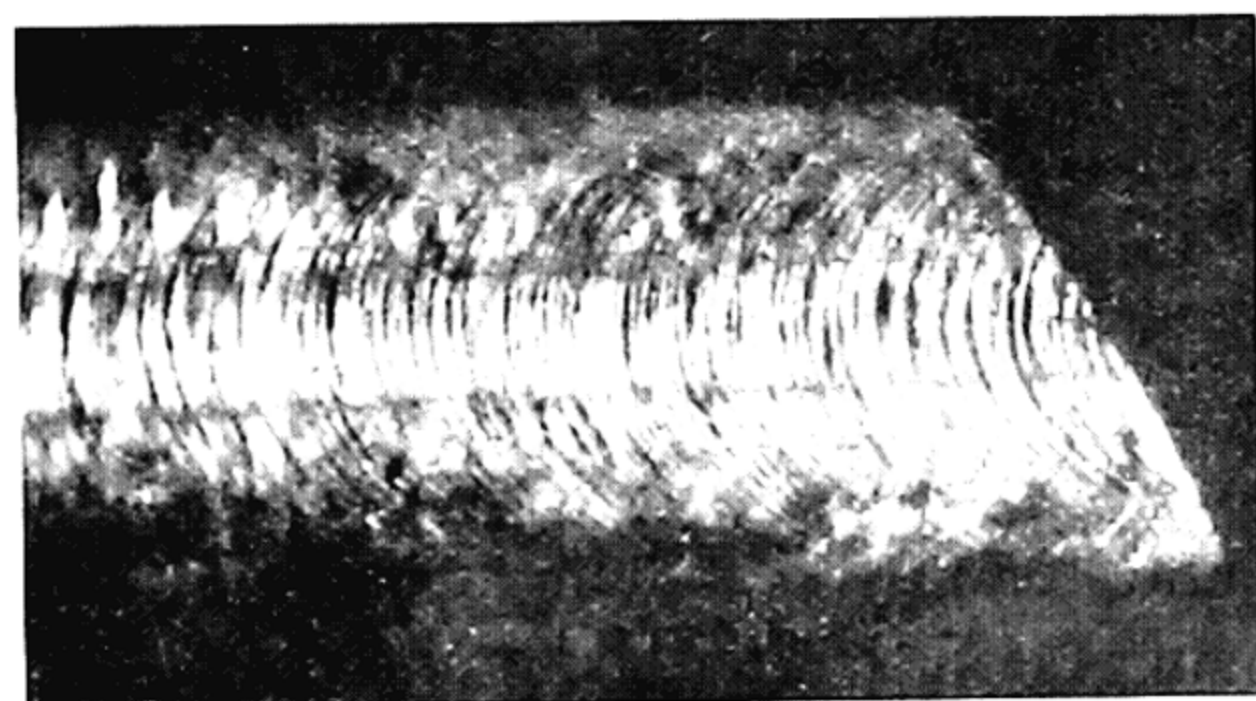


Figure 6. Glide planes on bismuth
at 264°C .

with the direction of pull (wire axis), twinning took place when the twinning plane made an angle of 45° with the wire axis. In this case both the old and the new glide planes are equally favourably placed for glide. How general this criterion may be is a matter for further investigation.

Mr Greenland and I have found that mercury at -180° twins much more readily

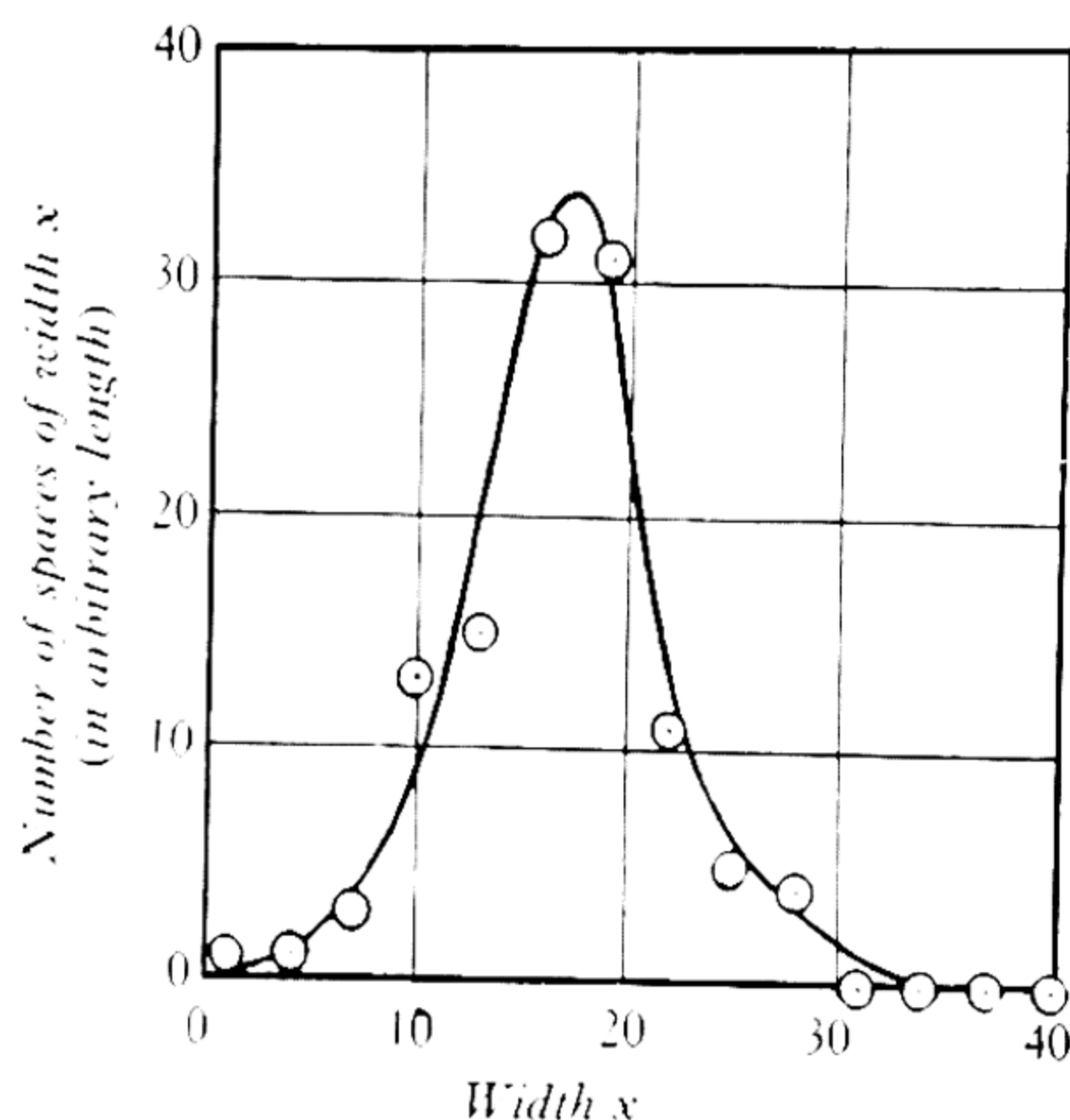


Figure 7. Distribution of spacing of glide planes in lead.

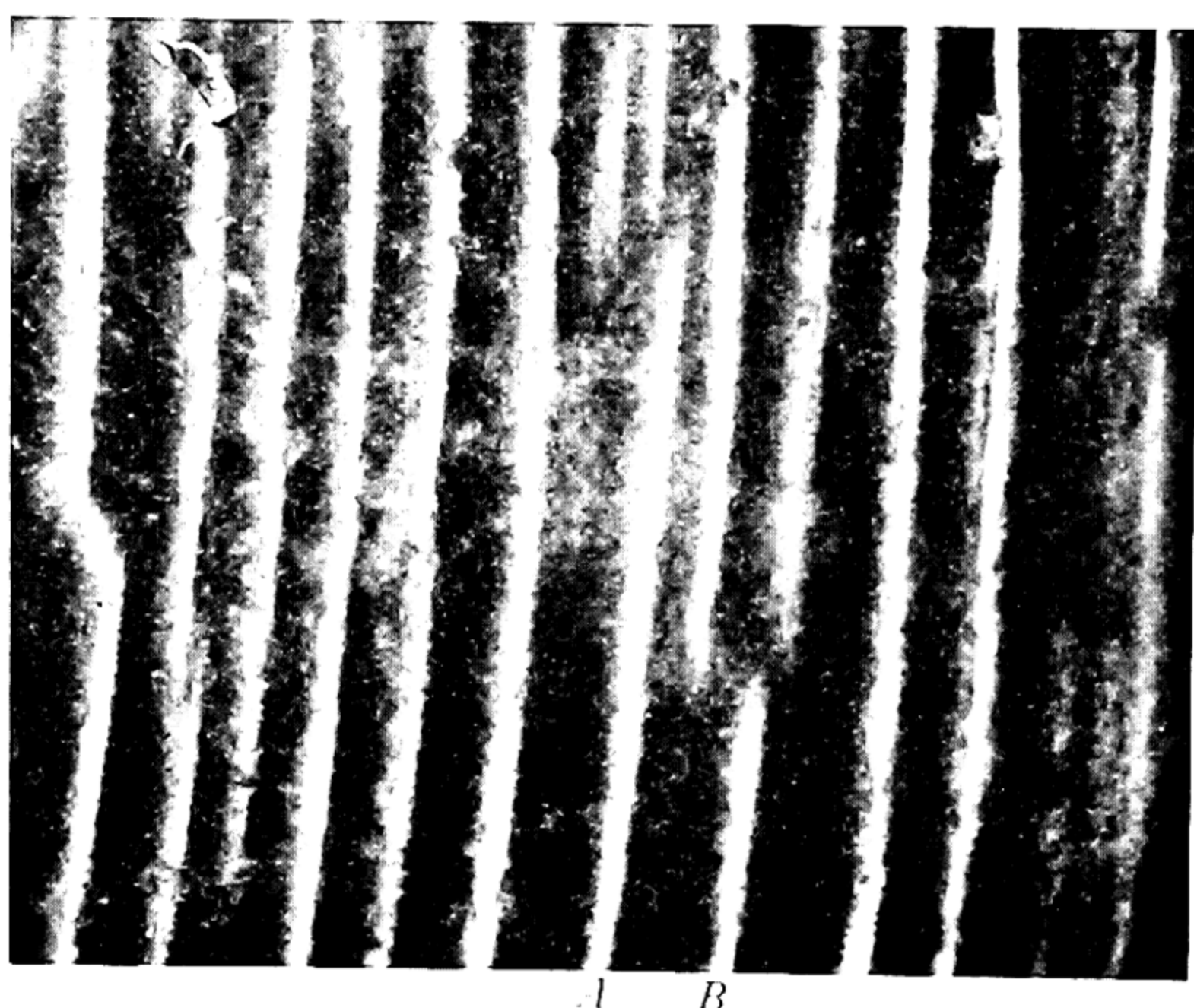


Figure 8. Slip lines in lead ($\times 800$).

and extensively than at -50° , with the characteristic "cry" (figure 5). This suggested that with rhombohedral metals, at any rate, glide takes place more readily at high temperature. Dr Roscoe and I therefore tried to produce glide in bismuth at a temperature 5° below the melting point, and procured a beautiful system of slip bands (figure 6), whereas at atmospheric temperature we found extensive twinning and no ordinary glide, in agreement with Gough and Cox⁽⁹⁾. This behaviour is in

direct contradiction to the examples quoted by Dr Schmid, of twinning, in preference to slip, at high temperature in zinc and cadmium, and shows how difficult it is to generalize in this field.

We have made measurements on the spacing of the glide planes. With mercury and lead the initial system of glide planes, when once developed, remains without addition for a considerable extension, although ultimately new bands appear between the old ones. The spacing of the planes is not constant, but has the ordinary chance distribution about a most probable value, as exemplified by lead (figure 7), where the most probable value is 4.2×10^{-4} cm.* Figure 8 shows the slip lines for lead, at a magnification of 850, and it is interesting to note how incomplete slip bands running from top to bottom terminate close to the ends of others running from bottom to top. This is strongly reminiscent of G. I. Taylor's theory of plastic deformation⁽¹⁰⁾ by the migration of faults, or centres of dislocation, under the influence of stress. The slip bands run slightly past one another, and where there are two bands terminating near the end of a band running from the opposite direction, the more distant of the two runs a little farther past (see figure 8, lines at *A* and *B*). It is to be further noted that the more widely spaced bands are complete. All this agrees with Taylor's calculation that the stress required to make one of two opposed bands run past the other is inversely as the distance between the bands. Taylor also calculates that the furthest distance by which two bands can overlap without running on completely is equal to the distance between them, which also appears to be roughly confirmed. The average spacing, too, is of the order demanded by Taylor's theory, viz. a few times 10^{-4} cm.

The spacing in lead is a real feature of the crystal, and has been found to be independent of the diameter of the wire, temperature of stretch (0° and 100°), rate of stretch (varied by a factor of 3000) and amount of extension, which suggests that it is due to a feature initially present in the metal, and not to a development of periodic anomalies by the action of the stress itself.

General conclusions from the experiments quoted are that critical shear stress is determined by surface imperfections, while plastic flow and plastic hardening are determined by internal flaws, variously called faults, crevices, or "Lockerstellen," to which metallic impurities segregate. It is suggested that, to comply with energy requirements, these impurities in all cases go to the sharp corners of both surface and internal cracks, where they can adapt themselves to the lattice and where they exercise a strengthening effect.

Finally, as regards the rotation of crystallites, discussed by Burgers, Chalmers and I⁽¹¹⁾ have shown by measurements of electrical resistance, and Gibbs and Ram Lal⁽¹²⁾, working in my laboratory, have shown by X-ray methods, that, when a polycrystalline wire of cadmium or of tin is extended, a rotation of the axes of the crystallites takes place. These metals show a hardening. On the other hand, with glass, which, as Joffé points out, shows no influence of plastic flow on mechanical strength, Ram Lal has found, by X-ray methods, that there is no rotation of the crystallites. I showed many years ago that polycrystalline wires flowing plastically

*¹Measurements of Dr Roscoe.

under constant stress eventually reach a stage where there is no hardening, i.e. where flow linear with time takes place. The X-ray experiments and electrical resistance experiments just quoted show that at this stage there is no progressive rotation of the crystallites. It is possible, then, that the intercrystalline boundaries can act in a way somewhat similar to that suggested by Burgers for the "cracks" in a single crystal, and produce rotation when there is a shear component along them.

REFERENCES

- (1) E.g. G. A. HULETT, *Phys. Rev.* **33**, 307 (1911).
- (2) *Phil. Mag.* **27**, 869 (1914).
- (3) *Z. f. Phys.* **54**, 16 (1929).
- (4) *Nature*, **133**, 912 (1934).
- (5) *Phys. Rev.* **45**, 324 (1934).
- (6) *Proc. Roy. Soc.* **145**, 699 (1934).
- (7) E.g. H. J. GOUGH, Marburg Lecture, *Amer. Soc. for Testing Materials*, **33**, Part II (1933), and H. J. GOUGH and H. L. COX, *J. Inst. Metals*, **48**, 227 (1932).
- (8) E. SCHMID and G. WASSERMANN, *Z. f. Phys.* **46**, 653 (1928).
- (9) *Proc. Roy. Soc.* **145**, 362 (1934).
- (10) *J. Inst. Metals*, **48**, 227 (1932).
- (11) *Proc. Roy. Soc.* **138**, 348 (1932).
- (12) *Phil. Mag.* **18**, 949 (1934).
- (13) *Proc. Roy. Soc.* **148**, 120 (1935).

Dr W. F. BERG. Prof. Andrade mentioned the problem of the plasticity of bismuth crystals. I want to report a few results obtained on this material. Bismuth crystals are shown by Georgieff and Schmid* to exhibit plastic deformation by slip. Later, Gough and Cox† and others were quite unable to find slip on bismuth crystals under similar stress conditions.

In my opinion this difference is due to the different methods of making the crystals. Georgieff and Schmid made their crystals under atmospheric pressure, whereas Gough and Cox made them *in vacuo*. I have applied both methods and the results of both papers were confirmed. Rough mechanical tests were made and the following results were obtained and published a short time ago‡:

(1) Crystals made in air show slip in tensile tests. Figure 1 shows clear slip lines on such a crystal. To show that the crystal has become a flat ribbon, part of it has been tilted 90° .

(2) On crystals made *in vacuo* no traces of slip could be detected in tensile tests.

(3) These crystals, however, exhibit slip bands in compression tests, where bigger stresses can be applied than in tensile tests. Figure 2 shows slip bands in the original crystal and in several mechanical twins, as described in *Nature*‡.

(4) Crystals made *in vacuo* are deformed by slip in tensile tests at higher temperatures (250°C). Figure 3 shows the two pieces of a crystal which was pulled apart. One part has been turned through 90° to show the typical deformation. There are two systems of slip lines, one of them due to slip in the $\{111\}$ plane and

* *Z. f. Phys.* **36**, 759 (1926).

† *J. Inst. Metals*, **48**, 227 (1932).

‡ *Nature*, **133**, 831 and **134**, 143 (1934).

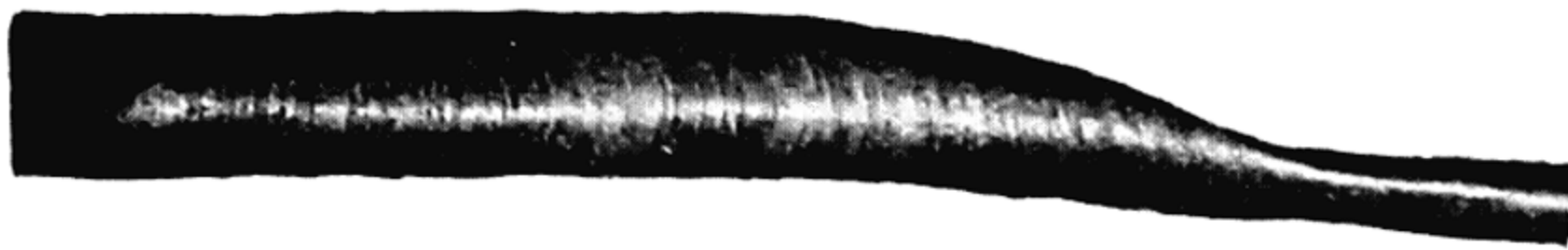


Figure 1.



Figure 2.



Figure 3.

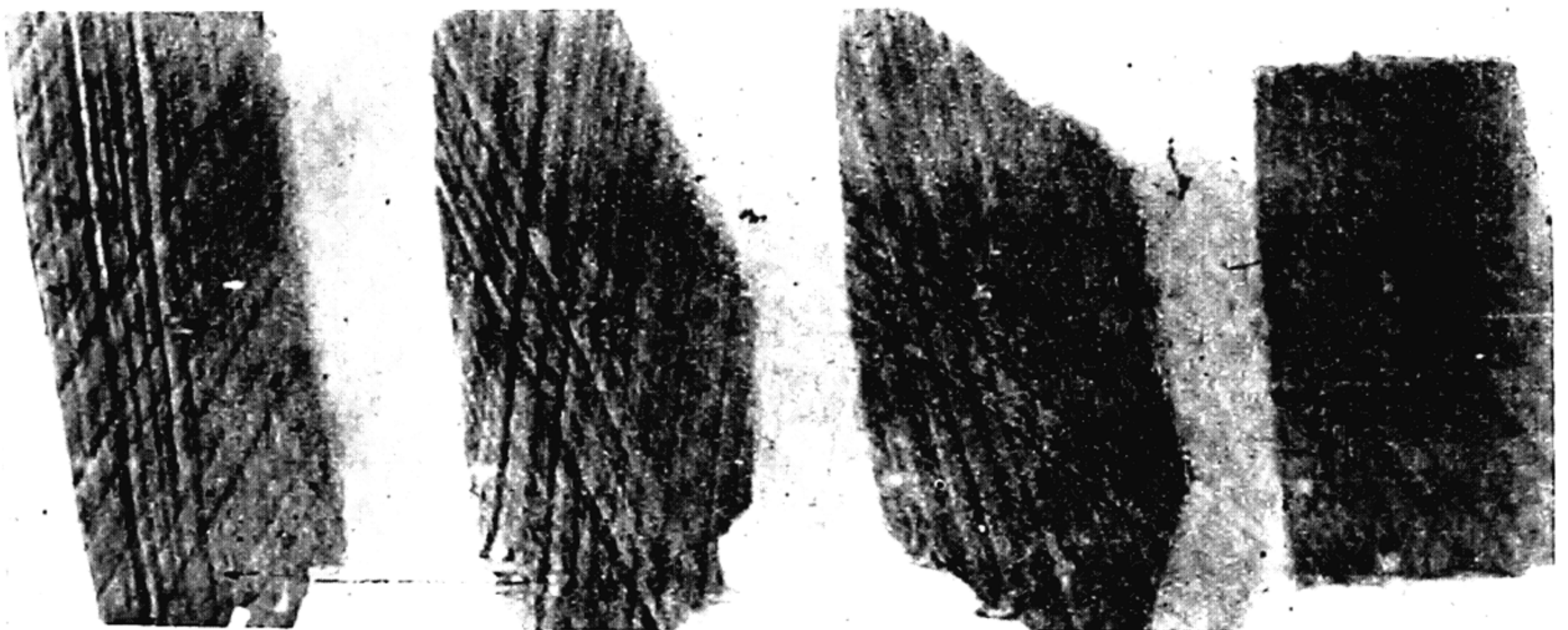


Figure 4.

the other either due to slip in the $\{11\bar{1}\}$ plane or to slip in the $\{111\}$ plane of a twinned part of the crystal.

According to a personal communication from Dr Gough (3) is confirmed by his latest experiments and it is interesting to hear that Prof. Andrade's experiments in which very pure material was used confirm (4) above.

The explanation why the crystals made in air are soft seems to be that they contain some of the gas which was used for cooling. Such crystals were heated *in vacuo* and a fair amount of gas came out. The amount was estimated by measuring the pressure obtained. There were about 3×10^{-4} molecules of gas per atom of bismuth in these crystals. This figure, however, still needs further confirmation. Besides this difference in the surroundings of the growing crystals, the other conditions (temperature gradient, velocity of growth) are also different for the two methods of growing metal crystals. Therefore the gas content need not necessarily be the cause or the only cause of the softness of the crystals made in air. But the results are interesting in so far as this seems a case where an *impurity* facilitates slip.

In connexion with the rotations which Dr Burgers has shown to take place in aluminium crystals if slip occurs, I wish to report a few results which were obtained on NaCl. The photograph (figure 4) shows four pictures of NaCl cleavage which were obtained by means of reflexion of X-rays from the cleavage. After one picture was taken the crystal was rotated 30° in the plane of reflexion. I shall not give the details of this method here*. It is only necessary to state that these pictures are images of the cleavage in so far as one point on the photograph corresponds to one point only on the reflecting surface, and that the images would appear to be evenly illuminated if the crystal were perfect. The black and white stripes correspond to traces of the slip planes on the cleavage and show that some rotation has taken place near the plane of slip. The axis of rotation lies in the plane of slip and is perpendicular to the direction of slip. This corresponds to the results of Dr Burgers and to those obtained earlier by Prof. G. I. Taylor and C. F. Elam† on aluminium crystals. But there seems to be a difference in the interpretation of these results. Dr Burgers assumes cracks to be inside the crystals and explains the rotation by the action of these cracks. If it is permissible to generalize from the results on NaCl, we may say that this explanation can hardly hold, for the following reason: the rotation obtained on NaCl seems to be fairly uniform along the whole plane of slip. This is seen on the photograph, which is about natural size. One can also grind off a small amount from the surface and find the same rotation on a certain plane of slip if one goes into the crystal. To explain these rotations by cracks seems to be impossible. We might try to assume that there are very many small cracks of the same size, but even then it seems hard to imagine how they can produce a nearly uniform rotation all along the plane of slip. At least in the case of NaCl, another explanation must be found.

Again, I do not want to raise objections to G. I. Taylor's explanation of plasticity of crystals and of strain hardening, which seems to be a great step forward. I merely want to point out that there are facts connected with deformation by slip

* See *Naturwiss.* 19, 391 (1931).

† *Proc. Roy. Soc. A*, 102, 643 (1923).

which still need further explanation. It may be that these facts are due to secondary effects.

There is the fact that we see slip bands at all. This fact means that two parts of the crystal have slipped one upon the other by a distance of several hundreds or thousands of atomic distances. We know that on NaCl crystals the occurrence of slip is marked by a stressed area along the plane of slip which shows itself by double refraction*.

Further, a fairly uniform rotation takes place in the neighbourhood of the planes of slip in NaCl.

I used to explain these facts to myself by a complete breakdown of the crystal, whose two parts slip one upon the other by a distance of many atomic distances. Since the crystals obviously consist of many smaller "mosaic" crystals (purposely no further details will be given of what is meant by this expression, but that there is something like it is clear from the X-ray experiments of Darwin and others) these smaller parts experience different strains and stresses according to their relative position with respect to the actual plane of slip. They are rotated, leaving a strained and stressed area along the plane of slip. Of course, the main question is still open: Why does such a breakdown of the crystal occur?

For single crystals of tin it is known that slip occurs according to the change of shape of the crystal, but that sometimes no slip bands can be detected. This may be a case in which slip occurs purely according to Taylor's theory. Perhaps an extension of this theory, incorporating some assumptions about the mosaic nature of the common crystals, might account for some hitherto unexplained facts.

Sir R. HADFIELD. The paper by Prof. E. Schmid contains information of a particularly interesting kind to the metallurgist. The evidence he shows, that the shear strength of crystalline materials is not greatly increased by lowering of temperature, would however hardly seem to be consistent with that obtained from other sources as concerning steel and iron, from which it is believed that the shear strength is more greatly increased by low temperature than the cohesive or direct tensile strength. Consequently, the weakness to shear which occurs at ordinary temperature is not displayed at low temperature, i.e. temperatures of the order of that of liquid air (-182°C.), and breakdown occurs at these low temperatures by direct tension rather than by shear. This explanation it is believed also accounts for the brittleness and lack of ductility of iron and most steels at low temperature, since shearing is necessary to ductility.

Prof. Schmid's remarks on twinning are also of particular interest to the metallurgical microscopist. The readiness of twinned areas to re-crystallize would seem to imply that twinning must be regarded as an actual crystal breakdown just as much as an actual state of strain by movement along the slip planes. It is clearly an abnormal condition which the regular forces of crystallization dislike and do their best to rectify when an opportunity occurs as by raising the temperature.

It is not clear whether his figure 5 represents calculated or experimental results

* I. W. Obreimoff and L. W. Schubnikoff, *Z. f. Phys.* 41, 907 (1927).

for the various metals shown, or whether the data obtained by these two methods are in agreement. Certainly the fact that nickel shows in this diagram a pronounced hardening effect is in agreement with my own observations on this metal. If theory is in agreement with experiment then it would appear that very useful progress has been made in knowledge as to the cause of work-hardening which is found of so pronounced a degree in manganese steel.

Prof. A. SMEKAL. In connexion with the very interesting paper by Schmid, I should like to mention that Miss Dommerich in my institute has recently given measurements on the critical shear stresses for all three different slip systems of rock salt at ordinary temperature, and that the fact that these shear stresses are independent of crystallographic direction of deformation has been very well established in this case⁽¹⁾. On the other hand, at much higher temperatures, Wolff was able to prove definitely the existence of gliding planes, which are in contradiction to the shear stress law⁽²⁾. Another interesting point which we have established on rock salt at ordinary temperature is a dependence of the operative slip systems on the form of cross-section of the monocrystalline rod. For instance, if we have to deal with tension perpendicular to a cube plane, four systems of dodecahedral gliding planes are equivalent. Nevertheless only those systems are realised for which the length measured along the gliding direction within the crystal is a minimum⁽³⁾. The origin for this new condition for slip is the fact that actual gliding starts from certain places within the crystal, and that the gliding planes tend to spread over the full cross-section with a definite velocity—facts which seem to be of great importance for all plasticity theories.

REFERENCES

- (1) S. DOMMERICH, *Z. f. Phys.* **90**, 189 (1934).
- (2) H. WOLFF, *Z. f. Phys.* **93**, 147 (1935).
- (3) A. SMEKAL, *Z. f. Phys.* **93**, 166 (1935).

Prof. E. SCHMID. I would like to add to the observations of Sir Robert Hadfield the following remarks which serve in the main to support his views.

(1) The fact that slip ceases in iron at low temperature does not compel the assumption that in this case the yield point rises particularly steeply with decreasing temperature. As Sir Robert remarks, the brittleness at -185°C . is caused by the fact that before the elastic limit is reached another mechanism enters (cleavage parallel to the (100) plane, mechanical twinning parallel to (112)*, with formation of cracks along this plane). The behaviour of iron thus demonstrates merely that the temperature change of these processes is less than that of the commencement of slip.

This receives a certain amount of confirmation from the scanty observational material at present available; the critical tension for tearing of bismuth and zinc crystals normal to the cleavage planes has been found to be independent of temperature.

(2) Examination of the atom distribution in the glide planes provides strong reasons for believing that the lattice is violently strained at the boundaries of twin

* W. Fahrenhorst and E. Schmid, *Z. f. Phys.* **78**, 383 (1932).

lamellae*. It is shown in this way, on purely geometrical grounds, that in many cases considerable distortion must occur.

(3) The hardening curves shown in figure 5 of my paper were determined experimentally. The first theoretical deduction of the curves was due to G. I. Taylor (reference (19) of my paper). According to his theory they should be parabolic, and in fact this is a good approximation to their form for the cubic metals.

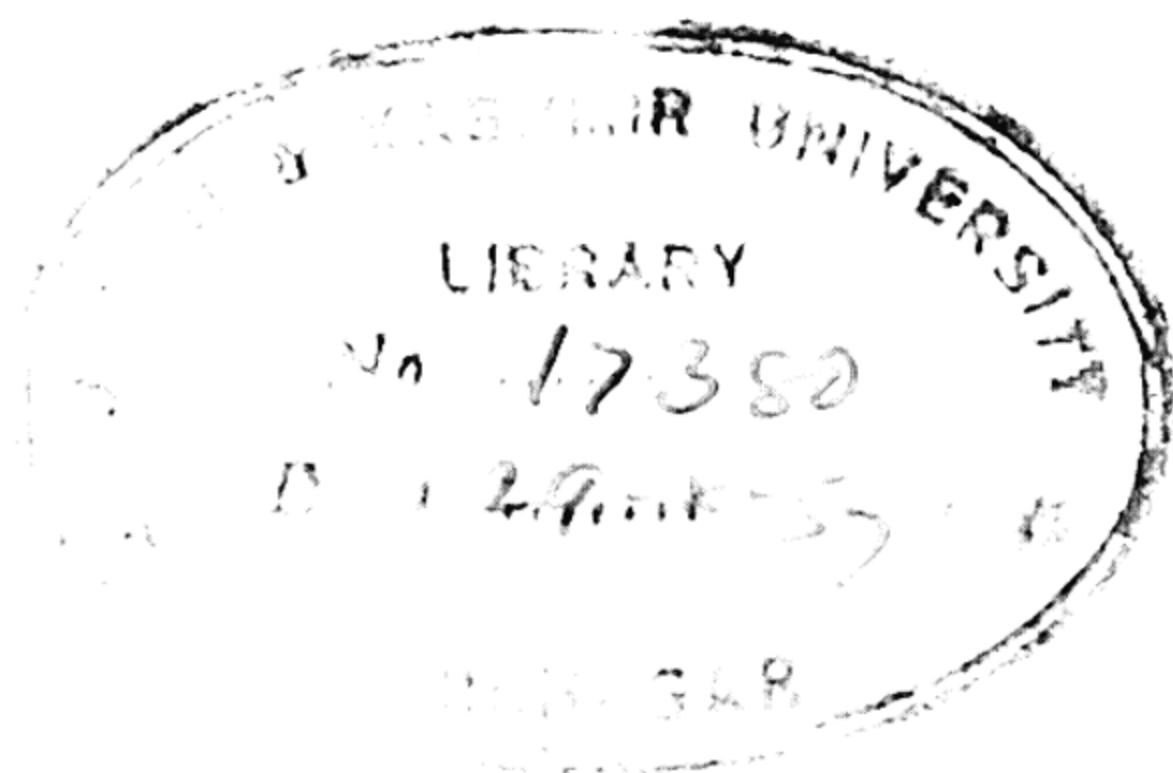
As regards the remarks of Prof. Smekal, Miss Dommerich's work has interested me particularly, as in it the shear-stress law is applied to the determination of the slip-elements ((100) planes), in the same way as was attempted previously for iron crystals†. It appears to me however that no absolute proof has yet been given that slip on (111) planes also occurs in rock salt at room temperature, nor in particular of the critical shear stress on the third slip system, in the strict sense implied by Miss Dommerich.

As to the statement of Mr Wolff that slip occasionally occurs in rock salt which does not agree with the shear-stress law, any expression of opinion must be deferred until the work is published. I shall here only remark briefly that in the case of tin crystals also, for certain initial orientations, a slip system is found to be operative which would not be expected from the known values of the critical shear stress. The reason for this must be the very marked hardening which occurs on the missing slip system with increasing slip, as a result of which a system becomes operative‡ on which the hardening is much less. A decision as to whether such an explanation also accounts for Wolff's rock-salt results will only be possible when we are in possession of the hardening curves, as yet unknown.

* See for example C. H. Mathewson, *Am. Inst. Min. Met. Eng.* (Feb. 1928).

† W. Fahrenhorst and E. Schmid, *Z. f. Phys.* **78**, 383 (1932).

‡ I. Obinata and E. Schmid, *Z. f. Phys.* **82**, 224 (1933).



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